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## Dredged Material Research Program



**TECHNICAL REPORT D-78-43** 

# PHYSICAL AND CHEMICAL CHARACTERIZATION OF DREDGED MATERIAL SEDIMENTS AND LEACHATES IN CONFINED LAND DISPOSAL AREAS

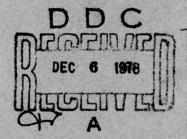
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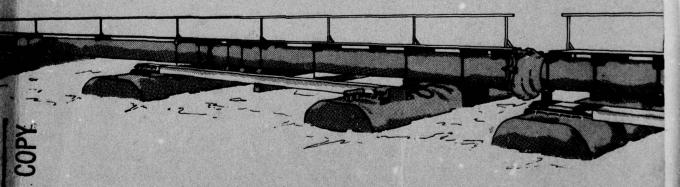
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> August 1978 Final Report

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U. S. Army Engineer Waterways Experiment Station P. O. Box 631, Vicksburg, Miss. 39180

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30 September 1978

SUBJECT: Transmittal of Technical Report D-78-43

TO: All Report Recipients

- 1. The technical report transmitted herewith represents the results of Work Unit 2D05 of Task 2D, Confined Disposal Area Effluent and Leachate Control, of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 2D was a part of the Environmental Impacts and Criteria Development Project (EICDP). This project was, in part, concerned with establishing a data base and evaluating potential pollution problems associated with different modes of dredged material disposal. The work units in Task 2D dealt more specifically with environmental impacts of confined land disposal of dredged material.
- 2. The overall objective of the Work Unit 2D05 study was to gather field data on the quality and quantity of interstitial waters and leachates from within, beneath, and down-gradient from four confined land disposal areas. Initially considerable background information on each site was obtained from the literature, personal contacts, and from concise field measurements. Factors deemed important in affecting the production and composition of leachates include: (a) dredged material composition, (b) composition of the adjacent and underlying soils, (c) hydrogeological conditions beneath the site (e.g., groundwater flow rate and pattern, geological formations encountered, and extent of groundwater regime), (d) climate, and (e) site-specific conditions (e.g., chemical and biological activities, soil moisture and precipitation patterns, pH, and Eh).
- 3. At each of the four field sites, ten sampling locations were usually established: four locations within the disposal area, four off-site monitoring stations down-gradient in the groundwater flow pattern, and two off-site stations up-gradient in the groundwater flow pattern for background data. Sediment and water samples were initially obtained from four depths. At locations within the disposal area, two sampling horizons were within the old dredged material. Each sampling station was hand bored and cored; sediment samples were collected at horizons later used for the collection of water samples. Samples were obtained from the unsaturated zone above the local groundwater table with ceramic cup soil water samplers, while groundwater samples were collected from plastic wellheads. Four sets of water samples were collected over a nine-month period.

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- The results of the study showed that leachate quality is a function of the physical and chemical nature of the disposed dredged material, site-specific hydrogeological patterns, and environmental conditions of the area surrounding the site (e.g., physical and chemical nature of the adjacent soils). In general, the study found that sodium, potassium, calcium, magnesium, chloride, total organic carbon, alkalinity, and manganese in leachates from disposal areas may impact local groundwater, especially if the water is used for drinking water or agricultural purposes. The data also indicated that low concentrations of cadmium, copper, iron, mercury, lead, zinc, nickel, and phosphate may reach groundwaters, but the levels should not pose water quality problems. Iron and manganese appeared to be produced by localized environmental conditions, and thus their mobility was not considered directly related to dredged material disposal activities. Certain sites showed localized high levels of certain contaminants, including nickel, cadmium, and copper. The highest levels for most trace metals were in off-site (monitoring and background) water samples, collected beneath an acid, poorly buffered salt marsh habitat. The major contaminants at the brackish water sites appeared to be the salts of major ions.
- 5. The data in this publication should be used, in context with past and future findings, for determining the impact of land disposal on groundwater quality. It is anticipated that these published results should aid those persons involved with criteria development, groundwater monitoring, environmental impact reports, permit programs, or other regulatory functions.

JOHN L. CANNON

Colonel, Corps of Engineers
Commander and Director

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ABSTRACT (Continued).

Twenty-six sampling devices were installed at each site with 12 on-site, 10 off-site, and 4 beneath the site. Water samples were collected four times in nine months; soil and dredged material samples were collected during the first sampling visit.

Analytical data show some significant increase in concentrations of chloride, potassium, sodium, calcium, magnesium, TOC, alkalinity, iron, and manganese in downgradient groundwaters. Concentrations of chlorinated hydrocarbons, cadmium, copper, mercury, lead, zinc, phosphate, and nickel were generally very low.

Results obtained from this limited monitoring period have shown some degradation of groundwater quality due to the upland disposal of dredged material. Additional data are needed to formulate guidelines for the selection of disposal sites with minimal environmental impacts.

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#### SUMMARY

When dredged material is disposed of in upland areas, the water quality impacts can be divided into two categories; the discharge of effluent slurries to surface waters, and the migration of leachates into underlying groundwaters. The purpose of this study was to evaluate the latter impact. This field study was conducted to evaluate the possible degradation of groundwater quality from confined upland disposal of dredged material.

Prior to site selection, a literature review and field investigation of prospective areas were conducted. This information provided the basis for choosing the four locations which best suited the goals of this study. The four sites selected for field investigation were Grand Haven, Michigan; Sayreville, New Jersey; Houston, Texas; and Pinto Island, Alabama. All available records pertaining to each site were examined, including: information such as historic, geographic, topographic and climatological data as well as, regional and site-specific hydrological data. Additional hydrogeological data were obtained in the field study.

A simplistic representation of the groundwater hydrology at each of these case study sites may be seen on Figure 69.

A comprehensive review of sampling devices and techniques was also performed. Vacuum/pressure lysimeters were chosen for interstitial water sampling and PVC well points for groundwater monitoring. In addition, by using specially constructed ABS sampling tubes, dredged material and soil samples were obtained from locations that would provide insight as to both lateral and vertical chemical and physical stratification. Twenty-six water samplers were installed at each site with 12 on-site, 10 off-site, and four directly beneath the sites. The ratio of lysimeters versus well points at each locality was determined by the specific hydrogeologic framework at the site. Four sampling visits were scheduled approximately every three months. Sampling and shipping techniques developed for the study were implemented during these visits.

The results from the analysis of on-site dredged material and off-site soils in relation to the examination of vertical and lateral differentiations, in general, failed to reveal any systematic

changes. For any particular parameter, both increases and decreases in values occurred in different locations as well as at different depths within each site. This is most likely due to the stratification caused by intermittent disposal operations.

Results of the particle size analysis of the dredged material suggested that the material in upland disposal areas is slightly more sandy than original bottom sediments. The reason for the difference might be due to the fact that finer particles tend to be carried with effluents to surface receiving waters due to turbulence and/or insufficient residence time.

Analysis of leachates and groundwaters indicate that potential adverse water quality impacts will most likely be due to the increases of chloride, potassium, sodium, calcium, total organic carbon, alkalinity, iron, and manganese. The extent of the potential impact was found to be a function of the physiochemical properties of the disposed dredged material, site-specific groundwater hydrogeological patterns, and environmental conditions of the area surrounding the site. The field monitoring of the case study sites generally revealed very low concentration levels of cadmium, copper, mercury, lead, zinc, phosphate, and nickel in downgradient groundwater.

In general, soluble phase sodium, potassium, and chloride were shown to have similar behavior. Dilution was the most important mechanism affecting the migration of these ions. Sodium and potassium might also be affected by ion-exchange reactions with the exchangeable ions held in the soil/dredged material. All three ions were shown to have affected the groundwater in at least one site.

Soluble phase calcium and magnesium were higher in the onsite dredged material samples than the off-site samples at two sites, indicating a potential for these two ions to migrate away from the site. Actual leaching of these two ions was also observed. Possible mechanisms regulating the transport of these two ions included ion exchange reactions with soil/dredged material, dissolution of nesquehonite and hydromagnesite for magnesium.

Levels of TOC and alkalinity were observed to have increased in groundwater below two of the case study sites. The transport of

alkalinity was probably regulated by biological oxidation and the dissolution/precipitation of calcite.

The soluble phase phosphate concentrations detected in this study were low, ranging from below the detection limit to a high of 0.91 mg/l (as P). The low level phosphate detected was probably due to adsorption onto clay particles. Although one of the case study sites had a higher phosphate average for the on-site samples than the off-site samples, there was no appreciable difference among the groundwater samples collected directly below the sites, downgradient from the site and upgradient from the site.

With the exception of manganese and iron, concentrations of trace metals in the leachate samples were mostly in the ppb or sub-ppb ranges. At such a low concentration range, solid transformation due to change in the redox condition, precipitation/dissolution, complexation, and adsorption were expected to play dominant roles in regulating their transport.

In general, in an aerobic environment, the stable solids that control the solubilities of these metal ions are oxides, hydroxides, carbonates, and silicates. Under reducing conditions, especially in saline sediments, most trace metals may gradually precipitate as sulfides with very low soluble concentrations in solution.

Adsorption could help account for the low levels of certain trace metals and chlorinated hydrocarbons in the soil/dredged material interstitial waters. The most important adsorbents included hydrated oxides of iron and manganese, soil organic matter and various clay minerals.

Total chlorinated hydrocarbons appeared to exist at higher levels in the dredged material than in off-site soil samples. This could be due to the accumulation of chlorinated hydrocarbons from industrial/domestic discharges into the waterways. The upper soil samples generally contained higher concentrations of chlorinated hydrocarbons than the samples obtained a few feet below. No soluble chlorinated hydrocarbons were observed in groundwater. It is expected that the chlorinated hydrocarbons that accumulated in the dredged material will not migrate away from the site.

The complexation effect usually accounted for the high levels of trace metals found in the soil/dredged material interstitial

waters. The major ligands responsible for complexation were chloride, organic species, hydroxide, carbonate, and sulfate.

The results of this limited study have shown that leachates from upland dredged material disposal areas have caused some degradation of underlying groundwaters. Due to the short duration of this monitoring effort, this conclusion can only be regarded as tentative. It is recommended that additional efforts should be directed to the formulation of guidelines for site selection. In order to achieve this goal, it will be necessary to carry out long-term extensive monitoring programs on the existing sites.

#### PREFACE

The work described in this report was performed under Contract No. DACW39-76-C-0171, entitled, "Physical and Chemical Characterization of Dredged Material Sediments and Leachates in Confined Land Disposal Areas," dated September 29, 1976, between the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, and the University of Southern California, Los Angeles, California. The research was sponsored by the Environmental Laboratory (EL), WES, under the Dredged Material Research Program (DMRP), Work Unit 2D05. The study was part of DMRP Task 2D, "Confined Disposal Area Effluent and Leachate Control," of the Environmental Impacts and Criteria Development Project (EICDP).

This report is the result of field studies designed to evaluate the effect of the disposal of dredged material in confined upland areas on the quality of downgradient groundwater.

The research was conducted under the supervision of Dr. K. Y. Chen, Professor and Director, Environmental Engineering Program, USC. This report was a basis for the dissertation of K. Y. Yu, who performed most of the laboratory and data analysis.

The field studies were performed by R. D. Morrison and J. L. Mang of SCS Engineers, acting as a subcontractor to USC in this study. Individuals who contributed to different portions of the laboratory operations were: N. McCamy, L. Bhatt, J. Stone, S. Kooklam, G. Sawtelle, T. P. Pan, and A. Z. Sycip. Individuals who participated in field investigations were D. Myers, T. Boston, K. Borgers and J. Tierney. Ms. C. McMahon performed the editing and typing. Special thanks are due Dr. P. Saint of California State University at Fullerton, Department of Environmental Studies, who served SCS as Hydrological Technical Advisor.

This contract was monitored by Mr. R. E. Hoeppel, Research Microbiologist of the EL, WES, under the supervision of Dr. R. M. Engler, Manager of the EICDP. Director of the WES during the period of this study was COL J. L. Cannon, CE. Technical Director was Mr. F. R. Brown.

### CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI) UNITS OF MEASUREMENT

U. S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

_	Multiply	Ву	To Obtain
	acres	4046.873	square metres
	Fahrenheit degrees	5/9*	Celsius degrees or Kelvins
	feet	0.3048	metres
	gallons (U.S. liquid)	3.785412	cubic decimetres
	inches	25.4	millimetres
	miles (U.S. statute)	1.609344	kilometres
	mils	0.0254	millimetres

<sup>\*</sup> To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: C = (5/9) (F - 32). To obtain Kelvin (K) readings, use: K = (5/9) (F - 32) + 273.15.

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# PHYSICAL AND CHEMICAL CHARACTERIZATION OF DREDGED MATERIAL SEDIMENTS AND LEACHATES IN CONFINED LAND DISPOSAL AREAS

#### PART I: INTRODUCTION

#### Need for Corps Research

- 1. Sediments serve as a respository of much of the heavy metals, pesticides, biostimulants, and other organic and inorganic waste released into waterways from municipal and industrial waste discharge, mining and agriculture activities, and other point and non-point pollution sources. The physical presence of sediments in waterways necessitates dredging of the deposited material. It has been estimated that in recent years the Corps of Engineers alone has dredged an average of 290 million m<sup>3</sup> of sediments annually from the Nation's waterways. About 65 percent of this is discharged into open-water sites away from shipping channels. The rest is disposed of on land usually within a dike structure. One of the major concerns of this activity is the possible degradation of quality of both surface and groundwaters in the proximity of the disposal area.
- 2. Normally sediment-bound pollutants are considered to be chemically stable and unlikely to be released to the overlying waters. Considering the extremely low levels of trace metals found in the present-day ocean, despite the continuous input from land sources, it would seem that sediments are the permanent sink of trace metals. However, a disturbance in environmental conditions may result in a shift in equilibrium affecting the mobilization of chemical constituents. Open-water disposal operations have been drastically reduced in recent years due to strict water quality legislation. This curtailment is occurring despite the results of many recent studies which indicate that the release of soluble contaminants during open-water disposal is minimal. It is anticipated that confined land disposal will be a rapidly expanding activity.

#### Problem Assessment

- 3. Little information is available concerning physicochemical transformations, migration, and fate of soluble contaminants associated with the disposal of dredged sediments in confined land disposal areas. This lack of scientific data is generating some concern on the possibility of both long- and short-term contamination of surface and groundwaters. Many questions exist regarding the migration and transport mechanisms of dredged sediment leachates.
- 4. During dredging operations, sediment and water are mixed, transported, and disposed of in open waters, or diked areas or on uncontained land areas. This process may result in the release or removal of metals and other toxicants, with the direction of transfer being determined by the redox and chemical conditions existing at the time. When dredged material is disposed on land it is subjected to oxidation by the mixing with oxygen-rich surface waters. Repeated oxidation and reduction, induced by air contact with the influent slurry and repeated wetting and drying of the sediments by precipitation, drainage, and evaporation, may promote a shortor long-term potential for contaminant migration in sediment leachates. A schematic of a representative active disposal site is shown in Figure 1.
- 5. Once leachate reaches the zone of saturation, it moves under the influence of gravity flow. Two flow systems influence the eventual path of the leachate. One is a local system that usually involves a fairly short travel distance, following the local water table contour to the nearest discharge point. However, some of the water may continue to migrate downward and enter the regional flow system. The regional system is usually at greater depths, passing under local discharge points toward major points of discharge. Therefore, leachate originating at a particular site could result in the pollution of both local and regional water. 6
- 6. Investigations of the generation, composition, and control of municipal landfill leachates have been conducted during recent years, primarily under the sponsorship of the Environmental Protection Agency. Most of the information generated is not

directly applicable to an understanding of leachate production from dredged sediments in confined land disposal areas because leachate production mechanisms and resulting leachate characteristics associated with dredged sediments are not comparable to those associated with municipal refuse leachates. Several significant contributing factors are:

- The composition and availability (release) of soluble constitutents in dredged sediments are markedly different from those in municipal refuse.
- $\underline{\underline{b}}$ . The moisture content of dredged material, in most cases, is much greater than that of municipal refuse.
- <u>c</u>. The field capacity and permeability of dredged sediments and municipal refuse are probably significantly different.

#### Objectives of the Study

- 7. Field studies are needed to determine if leachates from dredged material present a serious threat to groundwater supplies or if soil attenuation offers adequate protection. There are several general factors affecting the composition of leachate and its production. The most important of these are:
  - a. The dredged material composition.
  - b. The climate.
  - c. Hydrogeological conditions beneath the site.
  - <u>d.</u> Site-specific conditions; e.g., chemical and biological activities, soil moisture, pH, Eh, and other characteristics.

These factors vary considerably from site to site.

8. The overall objective of this study was to gather field data on the quality and quantity of interstitial waters and leachates from within and beneath active confined land disposal areas, together with background hydrochemical data, to determine the pollution potential of contaminated materials resulting from subsurface vertical and horizontal leaching. Specifically, objectives

were:

- a. To monitor the leachate and groundwater quality at four dredged material confined land disposal areas on four different occasions over a 9-month period. Water samples were to be analyzed for trace metals, chlorinated hydrocarbons, nutrients, and other parameters. These data were to be used to determine:
  - (1) Time-dependent changes in leachate quality at different depths.
  - (2) Effects of soil attenuation of mobile constituents.
  - (3) Changes in soil moisture.
  - (4) Groundwater dilution of leachates.
- b. To perform a detailed physical and chemical characterization of dredged sediment and subsoil core samples at all sampling sites. These data were to be used to define:
  - (1) The pollution potential of contaminated dredged sediments.
  - (2) Transport mechanisms responsible for the migration of contaminants.
  - (3) The magnitude and extent of contaminant migration from dredged material containment areas.

#### PART II: EXPERIMENTAL

#### Grand Haven, Michigan

#### Site Description

- 9. The Grand Haven, Michigan, site provided an excellent opportunity for investigating the migration of leachates from an upland disposal area situated in a freshwater hydrologic regime. Distinctive and pertinent characteristics are listed in Table 1.
- 10. The dredged material disposal facility at Grand Haven, Michigan, is located near the eastern shore of Lake Michigan on the north banks of the Grand River. The Grand River empties into Lake Michigan approximately 1 mile downstream. The regional map (Figure 2) shows the location of the site in relation to the Grand River and Lake Michigan.
- 11. The Grand Haven site covers about 2.4 ha (6 acres) which have been diked, resulting in a roughly rectangular configuration. The northern side of the site which measures 168 m (553.8 ft) is bordered by open land; the east by land owned by Verplank Coal and Dock Company. The southern edge of 181 m (594 ft) is set back from the Grand River by about 60.9 m (200 ft). The western edge is offset from an area of low relief, referred to as the Sag, by 53.6 m (176 ft); the area between the site and the Sag is marshland.
- 12. The dike which encloses the site is an embankment consisting of a core of concrete/asphalt slabs from demolition work in the area. The dike has measured heights ranging from 45 m (15 ft) on the southern extremity to 5.4 m (18 ft) along the north (as measured December 4, 1976). Additions to the existing berm were made during April, when newly dredged material was placed in the fill; dredged material from within the site was draglined for use in the construction of this addition.
- 13. Depth of the dredged material, as determined during borings on December 4, 1976, was fairly uniform, ranging from 1.8 to 4.2 m (6 to 8 ft). The site map (Figure 3) shows the locations of these corings, labeled MA to MJ.

- 14. Dredged material removed by the Corps of Engineers from Grand Haven Marbor has been deposited at several disposal sites in the vicinity. The study site was offered to the Corps by Verplank Coal and Dock Company in 1970. Since the land was in a swampy area and of no commercial value in its natural state, the Corps issued a permit to fill the site; filling has been taking place since 1972 (personal communication, 2 November 1976, Ross Kettleman, Chief Engineer, Corps of Engineers, Grand Haven Area Office). 7
- 15. Prior to its filling with dredged material, the site was characterized by a freshwater marsh flora and fauna; remnants are visible in the strip of land adjacent to the eastern edge of the fill. This area is inundated with water during the spring, when the snow melt drains to the harbor.
- 16. This former degraded marsh will probably be used for industrial purposes, depending upon zoning ordinances for the area, when it is filled.

#### Hydrological Characterization

- 17. Site investigations and information gathered during the literature search provided a composite of the total hdyrologic system in the Grand Haven area. Table 2 lists the dates of the various field trips and the specific hydrological tests conducted during each visit.
- 18. The total hydrological system at the Grand Haven case study site is characterized in terms of:
  - a. Climatological environment.
  - b. Surface waters.
  - c. Groundwater.

Site-specific field testing and accepted hydrological procedures, as well as a literature search, were employed to accurately define the nature of each of these systems.

#### Climatology

19. Historical climatological data for the region were obtained from the weather station at the Muskegon County Airport, approximately 16 km (10 miles) north of Grand Haven. Precipitation, temperature, relative humidity, and mean hourly wind speed recorded at this station during a 36-yr period, 1931 to 1966, are tabulated

on Table 3.8 A more detailed day-by-day record of precipitation and temperature extremes, and wind speed are included in Appendix A; the dates upon which field visits occurred are indicated by brackets.

#### Surface water

- 20. Surface water in the immediate vicinity of the Grand Haven disposal site normally filters through highly permeable sands of the area to a near-to-surface perched groundwater table; other surface waters drain to and accumulate in several drainage ditches, one being east of the site, which diverts runoff into the Grand River (Figure 3). Surface drainage flows from the higher elevations north of the site to the vicinity of the Grand River in the south.
- 21. Drainage within the diked area of the site flows from north to south and empties into the Grand River through several drainage pipes. Dredging and the subsequent leveling of the dikes during April of 1977 integrated on-site surface drainage patterns into the normal patterns for the area (surface runoff entering the site from the north and emptying into either of the drainage ditches) (Figure 3).
- 22. The Grand River is a major surface water body and acts as a discharge area for the shallow groundwaters in the vicinity of the site. The absence of major tidal fluctuations in Lake Michigan, into which the river flows, suggests that tidal differences would scarcely affect groundwater gradients. In order to quantify the degree to which the tide could affect flow patterns, on November 4, 1976, three 3.1-cm (1½-in) metal well points (M4, M8, M1) were installed in a triangular configuration on the perimeter of the site. This trangulation provided the field team with a gross understanding of the suspected flow patterns at the site. Six additional well points were driven, on-site and off-site, into the shallow groundwater to further define the flow patterns (Figure 3). All well points were surveyed and absolute elevations obtained. Recordings were obtained from these wells at various time intervals to coincide with tidal variations.
- 23. When the nine well points had been installed and surveyed, a series of water level readings were taken at each well for a 7-hr period; measurements were recorded on an hourly basis. An

identical test was conducted on April 6, 1977, to ascertain whether tidal or elevation differences in the Grand River influenced groundwater gradients. Measurements on both test days indicated that the river stage caused no noticeable change in the water level surface; this trend was observed on all five trips in which water level measurements were taken.

25. The effect of wind chop or standing waves in Grand Haven Harbor on groundwater patterns immediately adjacent to the riverbanks was not indicated by any of the constructed water table maps.

#### Groundwater

- 26. Characterization of the groundwater flow patterns at Grand Haven was determined by hydrologic investigations in three areas:
  - a. Visual investigation of surface features.
  - b. Water level readings from the network of nine well points and twelve monitoring wells.
  - c. An off-site pumping test.
- 27. An attempt was made to identify those surface features which could provide signs of groundwater characteristics. The drainage ditch illustrated in Figure 3 and the designated marsh areas were studied. The area south of the site on the Harbor River showed that the Grand River acted as a point of discharge for the shallow groundwater, suggesting that this groundwater, in the immediate vicinity of the fill, was flowing towards the Grand River.
- 28. Phreatophytes with shallow roots were noted at the site, which indicated a shallower depth to the groundwater in the southwest. The lack of this same vegetation in the north suggested greater groundwater depths in the north and northeast. Surface vegetation provided an indication as to the most advantageous areas for installing the previously mentioned metal well points.
- 29. The well points designated M1 to M9 (Figure 3) also acted as monitoring stations for defining the groundwater flow near the site. A series of five water level readings, corresponding to the five sampling visits, were recorded. The results of these measurements are portrayed in the water level contour maps in Figures 4 through 8. The first three maps show that the groundwater

flows from northeast to southwest; a less pronounced gradient within the fill was due to the deposit of dredged material in April and was responsible for the change in contours in the last two maps.

#### Pumping tests

- 30. A pumping test, designed to provide information concerning the characteristics of the shallow groundwater system, was the third element of the hydrological investigation. Both on- and off-site pumping tests were originally planned but the on-site tests were unsuccessful, because the dredged material yielded little water at a pumping rate of 151 % (40 gal) per minute. Therefore, further attempts at an on-site pumping test were curtailed.
- 31. Off-site pumping and monitoring wells were drilled on December 4, 1976, and designated MP and MO, respectively. The location of these wells, situated north of the site to minimize any effect on the Harbor River, is shown in Figure 3. Construction and depth of the wells, as well as the lithology in which the well screens were placed, are depicted in Figure 9.
- 32. The off-site pumping test was conducted on August 4, 1977; results are illustrated in Figures 10 and 11. An average coefficient of transmissibility value of 10,490 gal/ft/day was calculated from the drawdown and recovery curves.

  Geology
- 33. The geology of the Grand Haven site is presented in terms of both the regional and site-specific geology in order to present both the macrogeologic and microgeologic systems affecting the site.

#### Regional geology

- 34. Grand Haven lies within the geologic province known as the Michigan Geologic Basin, a synclinal depression filled with Paleozoic-aged sediments. In the general area around Grand Haven, most of these sediments consist of lower Mississippian formations composed primarily of sandstone, shale and limestone. 10
- 35. Figure 12 illustrates the relation of these series to others in western Michigan. The glacial drift deposits are primarily clays, silts, sands, and gravels, extending to a depth of 60 to 274 m (200 to 900 ft). The Marshall formation (sandstone,

siltstone, and shale) which underlies these glacial deposits is the major bedrock in the Grand Haven area.  $^{11}$  In many parts of Michigan this formation provides a major source of water from the fractured sandstone horizons.

#### Site geology

- 36. Site geology is typical of the glacial deposits in this part of Michigan. In all the on- and off-site borings, indigenous soils of fine sand were contiguous to a depth of 6 m (20 ft) where a dense clay stratum was encountered.
- 37. On November 4, 1976, this layer of clay was identified in a resistivity survey using a Wenner spacing configuration. Figure 13 shows the location of the survey profile north of the site (R1 to R).
- 38. The soil column for the Grand Haven area (Figure 13) shows a typical sequence of fine to coarse sands over the clays. The clay layer is reportedly several hundred feet thick, as derived from nearby well logs and on-site boxing logs (Appendix B). The fence diagram in Figure 14 was constructed from on- and off-site well logs and illustrates the uniform clay layer under the site.

#### Sayreville, New Jersey

#### Site Description

- 39. The physical setting at Sayreville, New Jersey, is listed in Table 4 and indicates its potential for study in a salt marsh area with pronounced tidal effects.
- 40. The dredged material disposal facility near Sayreville, New Jersey, is located in the eastern part of the state on the southern banks of the Raritan River, which empties into the Atlantic Ocean several miles to the east. Raritan Bay is approximately 1.6 km (1 mile) downstream from the site (see Figure 15). The disposal site is located at the head of a small peninsuls bordered by the river.
- 41. Relief in the immediate vicinity of the site is fairly level; the site itself is an approximately 17-ha (44-acre) slightly elevated diked area with a roughly rectangular configuration. The north side of the site (513.7 m or 560 yd) is bordered by the Raritan River, the west side (596.3 m or 650 yd) by U.S. 9, the east side (348.6 m or 380 yd) by New Jersey Highway 35, and the south side

(435.7 m or 475 yd) by a vacant lot adjacent to Amboy's Drive-In Theatre.

- 42. The dike that encloses the site is an earthen embankment approximately 5.1 m (17 ft) high. The outer dimension on November 28, 1976 was 8.2 m (27 ft) from the surrounding land to the top of the berm, while the distance from the top of the berm to the dredged material within was 3.0 m (10 ft) on the same date. Depth of the dredged material fluctuated between 6.0 m (20 ft) and 7.6 m (25 ft), as determined by on-site borings on November 2 and 3, 1976 (Figure 16). The material within the enclosure is fairly level, interrupted only by a small baffle dike (Figure 17).
- 43. Berm height has been increased throughout the life of the site, most recently in April 1977. There have been intermittent dredge and fill operations, as well as additions to the dike.
- 44. The Sayreville, New Jersey, disposal site is owned by National Lead Industries. Their titanium oxide plant, which operates the site and three other disposal lagoons in the general vicinity, is located approximately 0.8 km (½ mile) east of the site; two of the disposal ponds are west of the site (see Figure 16).
- 45. Before filling, the land was a salt marsh; remnants of these wetlands are still visible to the east and southeast. The phreatophyte Phragmites communis is the major flora species in the marsh. 13
- 46. The lowlands east of the case study site are inundated daily by the 1.5 m (5.0 ft) mean tidal range of the Raritan River, although the disposal area itself is free from this tidal inundation as well as from flooding.  $^{14-16}$  Hydrological Features
- 47. The hydrological system at Sayreville, New Jersey was characterized via a series of site investigations using data from field investigations in conjunction with hydrological information gathered during the background literature search. Table 5 lists the dates of the various field investigations and the specific hydrological tests.
- 48. The results of these investigations are categorized in terms of three subject areas:
  - a. Climatological environment.

- b. Surface waters.
- c. Groundwater.

These sources provided information that accurately defined the nature of each of the components at Sayreville, New Jersey.

#### Climatology

49. Historical climatological data for the region was obtained from the weather station at Newark Airport (approximately 32 km (20 miles), north of Sayreville (see Table 6). Precipitation, temperature, relative humidity, and mean hourly wind speed were recorded; data are based upon a 36-yr period, from 1931 to 1966. A more detailed day-by-day record of the same elements is included in Appendix C; the dates of the field visits are indicated by brackets.

#### Surface water

- 50. Surface waters are a major influence upon the hydrological system at Sayreville. Because of the large artificially impermeable area (e.g., asphalt paving at the nearby theater, roads, etc.), the majority of the average annual 115 cm (45 in) precipitation in the immediate vicinity is channeled into drainage ditches that direct the surface runoff directly into the Raritan River or into the nearby salt marsh east of the site (Figure 16).
- 51. Surface water within the diked area of the site flows from south to north forming shallow ponds in the lower areas and finally draining through either of the 2 cm (18 in) discharge pipes (Figure 17). This phenomenon was observed during field investigations on November 4 and 28, 1976. The position of the effluent pipes implies that the on-site surface water drainage pattern has been constant throughout the history of the site.
- 52. The Raritan River has a pronounced effect upon the hydrological system of the Sayreville, New Jersey, site. According to tide tables published by the U. S. Department of Commerce, the mean tidal range in the vincinity of the site is 1.5 m (5 ft). This surging of waters through the salt marsh reverses the normal hydraulic gradient through the wetlands in the immediate vicinity of the river.
  - 53. In order to determine the impact of the tide upon ground-

water flow patterns, three 3.1 cm (1½ in) diameter metal well points (NJ3, NJ7, and NJ6) were installed in a triangle around the site and surveyed to relative elevations. Measurements from these wells provided the field team with the necessary information for a gross understanding of the groundwater flow patterns. Seven additional well points were driven into the shallow groundwater on- and off-site to further define these patterns (Figure 17).

- 54. Well points installed on November 2, 1976, along the northern rim of the site (NJ3, NJ4, NJ5, NJ6, NJ7) were specifically located to quantify the tidal effect. The top of the well points and subsequent monitoring devices were surveyed by SCS personnel from Reston, Virginia, to provide the field team with relative measurements for developing isopotential water level maps. All surveying was accomplished within a second order of traverse. Also, three bench marks were located on-site to assist the surveying during subsequent field visits to the monitoring/sampling wells.
- 55. On November 11, 1976, a series of water level measurements from this well point network were obtained over the course of 5 hr. Groundwater contour maps were then constructed to determine the effect of tidal inundations upon groundwater flow patterns. None of the on-site wells were dramatically affected by the tidal cycle; the extent to which water levels in the off-site wells were affected was directly related to the wells proximity to the Raritan River. Interference by winds that could have disrupted the tidal range was not a factor during the measurements recorded on November 11, 1976. 15
- 56. Figures 18 through 23 illustrate the changing configuration of the water level contours developed from measurements obtained on November 11, 1976. Analysis of these contours provided the field team with the data necessary to determine the optimum location of the monitoring/sampling wells and pumping wells.

#### Groundwater

- 57. Groundwater flow patterns at the Sayreville case study site were determined by:
  - a. Visual investigation of surface features.
  - b. Water level readings from the network of

well points.

c. An off-site pumping test.

The following discussion on groundwater is a result of the field findings from these investigations.

- 58. On November 2 and 28, 1976, an intensive inspection of the Sayreville case study site determined the surface features which were, perhaps, indicative of subsurface groundwater contours. The drainage ditches, marsh areas, baffle dikes, and other features noted are illustrated in Figure 17. Water was observed seeping through the earthen dam into the surrounding marsh and/or drainage ditches, as illustrated in Figure 24. The cross-sectional area, labeled  $^{\rm A}_1$ -1 may be seen on the eastern segment of the site in Figure 24.
- 59. Leakage from the site was observed along the entire length of the dike, providing the first indication that the fill acted as an effluent or recharge source to the surrounding groundwaters. Later, data from the on-site wells demonstrated that this seepage corresponded to water levels within the fill.
- 60. There were phreatophytes adjacent to the fill and surface manifestations of groundwater seepage near the Raritan River. Structures that could possibly impede the flow of groundwater, road embankments, bridge foundations, etc. were studied and noted. This preliminary field survey provided manifestations of possible groundwater characteristics.
- 61. A network of 10 metal well points installed on November 2, 1976, and 10 monitoring/sampling wells installed November 28, 1976, provided a comprehensive monitoring network for identifying the groundwater flow patterns both on-site and in the immediate vicinity. A series of four water level readings were recorded during field monitoring visits to the site. The results of these measurements are depicted in the water level contour maps (Figures 25 through 28) for each of the four sampling periods. These readings were obtained on November 28, 1976; and April 6, June 2, and August 3, 1977. Measurements were also obtained on November 2, 1976, but could not be used to construct a contour map, since water levels had not stabilized sufficiently for representative

readings. This condition was due primarily to the low-yielding characteristics of the clays.

- 62. The on-site contours of 31.5 m (105 ft) in Figures 27 and 28 were the result of the complete ponding of the site from recent dredging. The standing water level was compared to known elevations of wells within the site in order to provide an approximate contour gradient value.
- 63. The water level contours indicated that groundwater patterns in the area were directly controlled by the dewatering at the disposal site; this recharge source is illustrated in the streamlines on each contour map which depict a generally radial flow from the site which was consistent throughout the project.

#### Pumping test

- 64. The third segment of the hydrological investigation, the pumping test, was designed to provide information concerning the shallow groundwater system and data on pumping time versus constituent concentration during pumping. Locations for the wells were based upon the extent of the tidal influence upon the groundwater. 17
- 65. Well construction, distances, and depths of both on- and off-site pumping and monitoring wells are illustrated in Figures 29 and 30. Efforts to perform a pumping test on-site were unsuccessful, because both the well and pump became clogged with dredged material. The results of the off-site pumping performed on August 4, 1977, are depicted in Figures 31 and 32. Using drawdown and recovery curves, an average coefficient of transmissibility value of 8264 %/m/day (7,161 gal/ft/day) was calculated. Geology
- 66. Geological characteristics of the Sayreville site are presented in terms of the regional geologic regime and site-specific geology. Regional geology will be presented first, so an understanding the the geology of the site in relation to the

#### Regional geology

general area may be understood.

67. The Sayreville site is in Middlesex County, New Jersey, which lies in two physiographic provinces, the Coastal Plain and Piedmont. The site itself is located within the Coastal Plain

Province and is characterized by unconsolidated sands, clays, and marls of Cretaceous age, with low-angle dips to the southeast. Sediments in the eastern segment of Middlesex County in the general vicinity of the site include nonconformities between the Upper Triassic Newark Group (predominantly shales and sandstone with interbedded volcanics) and the upper Cretaceous Raritan River formation, composed predominantly of unconsolidated sands, clays and greensand marls. <sup>18</sup> In several areas, the Pensauken Formation of Quaternary age is visible, capping the hills south of the site and exposed in the river valleys. Where the Raritan River has cut through the river valley, a formation of alluvium as been deposited by the meandering river (see Figure 33).

## Site geology

- 68. Site-specific geology follows the general pattern for the regional geology of river valleys. The case study site is in an area of river deposition at the mouth of Raritan Bay. Indigenous soils are derived from the flooding of the Raritan River, as well as normal erosional deposits from the nearby hills. The resulting sequences, as depicted in the soil column in Figure 34, are a series of interbedded sands, silts and clays; the soil column was derived from boring logs compiled and indexed in Appendix D. These on- and off-site borings provided the basis for the fence diagram (Figure 35) that also illustrates the relation of the water levels to on- and off-site land. A stratum of clay encountered in NJP3 and NJP4 appeared to be a discontinuous lens.
- 69. No major surface or subsurface anomalies were seen in the alluvial materials. Lack of surface evidence, coupled with the geological literature, indicate that the general area is seismically inactive. <sup>18</sup>

# Houston, Texas

## Site Description

70. The dredged material disposal site near Houston, Texas, was chosen as a case study site because it is characteristic of a highly contaminated upland disposal area in a wet, humid environment. Also it represented an inland site, located about a mile (1.6 km) from the ship channel. Table 7 lists the physical characteristics identified at the start of the project and confirmed

at a field investigation on November 2, 1976.

- 71. The Houston site, known as the Clinton Disposal Site, is owned and operated by the Galveston District, U.S. Army Corps of Engineers, and is located approximately 8 km (5 miles) east of Houston, Texas, between Galena Park and Pasadena. The land was formerly marshland (Figure 36). The 226 ha (560 acre) site is rectangular, approximately 1,295 m (4,250 ft) by 1,981 m (6,500 ft) and is roughly bisected by Mercury Road which links Galena Park to Pasadena (Figure 37). Surrounding land use is primarily urban, although there is some open land to the east.
- 72. The dike that encloses the site was constructed of indigenous materials by the Corps and varies from approximately 3.6 to 4.5 m (12 to 15 ft) in height, and 9.1 to 12 m (30 to 40 ft) in width at the base. Extensive additions were made to the levees in March 1967 when material was added to the outer base of the dike for erosion control.
- 73. Only the eastern half of the Clinton Disposal Site, approximately 111 ha (275 acres), was studied for this report; the total site was simply too large (226 ha or 560 acres).
- 74. The southeastern corner of the study area, approximately 4.6 to 6.0 m (15 to 20 ft) higher than the rest of the acreage, did not show the ponding visible elsewhere on visits on November 6 and December 7, 1976. As determined from on-site borings, the depth of the dredged material in this section ranged from 6 to 7.6 m (20 to 25 ft). Figure 38 shows the location of the ten corings, labeled monitoring devices (HA HJ), as well as the two wells (ONPW and ONOW) drilled for the on-site pumping test.

## Hydrological Features

- 75. Background information pertaining to both regional and site-specific hydrological features was solicited to augment the data collected from the specific hydrological studies performed as listed in Table 8. The total hydrological system at the Clinton Disposal Site is described in terms of:
  - a. Climatological environment.
  - b. Surface waters.
  - c. Groundwater characterization.

## Climatology

76. Historical climatological data for the region was obtained from the weather station at the Galveston Post Office, approximately 40 km (25 miles) south of the site (Table 9). Precipitation, temperature, relative humidity, and mean hourly wind speed were recorded at this station for a 36-yr period, 1931 to 1966. A more detailed day-by-day record of precipitation and temperature may be found in Appendix E; the dates upon which the field visits took place are indicated by brackets.

## Surface water

- 77. Surface waters in the vicinity of the site drain through creeks and drainage channels to the Houston Ship Channel, approximately 3.2 km (2 miles) to the south. The drainage ditch north of the site also empties into this channel (Figure 37).
- 78. On-site surface drainage from precipitation and dewatering flows to the northern portion of the site due to normal topographic gradients, and subsequently collects in a pond as observed during sampling visits. The ponded water flows through a 1.3-m (4½ ft) pipe into a drainage ditch, which empties into Hunting Creek 0.8 km (0.5 mile) east of the site and then into the Houston Ship Channel (Figure 37).
- 79. The Houston Ship Channel is the nearest large body of surface water. Its distance from the site and the subsurface nature of the soils preclude any tidal interference with the on-site groundwater.

#### Groundwater

- 80. The groundwater characteristics of the Clinton Disposal Site were determined through:
  - a. Visual investigation of surface features.
  - <u>b</u>. Water level readings from the network of well points and monitoring wells.
  - c. On- and off-site pumping tests.
- 81. On the visits of November 6 and December 12, 1976, an effort was made to identify those surface features which would indicate groundwater characteristics. Both the drainage ditch and the dike along the northern perimeter of the site were studied.

Shallow borings on either side of the ditch indicated that the surface waters flowing eastward were perched upon impervious clays. Inspection of the dike at the northern border of the disposal area exhibited no seepage from the on-site ponded waters; exposed sections of the soil at road cuts and ditches around the site provided no evidence of springs or seepage. Other visible indications of near-to-surface groundwater such as phreatophytes (e.g., willows and salt cedar) were also studied.

- 82. Twelve 3.1-cm (1¼ in) diameter metal well points were installed on November 6, 1976, on- and off-site, to identify base-line groundwater flow patterns and thus provide a comprehensive shallow groundwater monitoring network; these wells, labeled H1 through H12, are shown in Figure 38.
- 83. Although the on-site wells intersected groundwater at relatively shallow depths (4.5 m, or 15 ft), all of the off-site wells were dry. Moreover, the compact nature of the native clays prevented the well points from being driven to a depth greater than 6 m (20 ft) at any location. As shown in Figure 38, the well points labeled H7, H8, and H9 were all located within 3.0 m (10 ft) of a drainage ditch. These wells, which were dry despite their proximity to the ditches, reinforced the earlier observation that the native clays provided an effective aquitard to surface infiltration from the drainage ditches.
- 84. Groundwater, assumed to be primarily from sediment disposal within the site and precipitation, was detected in each of the eight on-site well points, the first indication that groundwater artificially introduced within the fill system was separate from deeper native aquifers.
- 85. Water level contours were developed from measurements taken from the on-site wells and monitoring devices illustrated in Figure 38. The contours followed the general topographical gradients within the site; the areas of highest hydraulic gradient corresponded to the vicinity where the dredged material was pumped onto the site, further suggesting that on-site contours are artifically produced as a result of disposal operations.
  - 86. Water level contour maps constructed from readings

obtained on the dates listed in Table 8 are depicted in Figures 39 through 43.

- 87. Subsequent drilling on- and off-site suggested that onsite groundwater was indeed independent of off-site systems. Water levels in on-site versus off-site wells and the results of the pumping test reinforced this conclusion.
- 88. The dense clays underlying the dredged material, as observed in the on-site pumping and observation wells (ONPW and ONOW, respectively), would act as an effective impermeable barrier and prevent large amounts of on-site water from infiltrating to the regional groundwater. It was not within the scope of this study to determine if such clays underlaid the entire Clinton Disposal Site.

## Pumping test

- 89. Wells for pumping tests were installed on- and off-site. The previously mentioned on-site wells (ONPW and ONOP in Figure 38) were drilled 10.6 m (35 ft) deep, with a 3.0 m (10 ft) well screen (Figure 44). Off-site pumping and monitoring wells, similarly labeled OFPW and OFMW, were drilled to a depth of 10.6 m (35 ft) where a thick layer of sand under artesian pressure was encountered. A piezometric head of 3.0 m (10 ft) was measured. Figure 45 illustrates the construction of these wells, as well as the lithology of the area in which they were placed.
- 90. When a second off-site pumping well (OFPW2) was installed north of the site, a thin stratum of water-bearing sandy clays was encountered at a depth of 9.7 to 12.1 m (32 to 40 ft).
- 91. An on-site pumping test failed, because the pump and hose clogged with dredged material; efforts on December 6, 1976, and March 25, 1977, were both unsuccessful.
- 92. A pumping test using off-site wells ONPW and ONOP was performed on December 7, 1976. Although the water in the wells was subject to artesian pressure, dewatering took place after only a few seconds of pumping at 151 & (40 gal) per minute. The time delay required for the well to become recharged, along with the rapid dewatering of the well, resulted in inadequate data. Similar results were obtained when a pumping test in well OFPW2 was attempted, suggesting that the water-yielding sands encountered

by both off-site wells represented isolated lenses of permeable deposits, rather than parts of a continuous aquifer. Well logs from nearby city wells suggested that no major aquifer existed for several hundred feet below ground surface. 19
Geology

93. Geologic characteristics of the Clinton Disposal Site are presented in terms of regional and site-specific geology.

## Regional geology

94. The Clinton Disposal Site is located in a sector of south-eastern Texas, which is part of the Gulf Coast geosyncline. This area is typified by reworked sediments which were deposited in the lowland areas. At depths of several thousand feet, the Beaumont and Lissie Formations, primarily shales and sandstones, are the predominant bedrock formations. The geologic map for this area (Figure 46) shows the area to have sediments of Quarternary age including both the Beaumont and Lissie Formations.

## Site geology

- 95. The geological setting at the site is similar to the general pattern of predominantly clayey sediments, which characterize this Gulf Coast geology. Soils encountered during off-site borings were essentially tight clays with some sands. Figure 47 shows a generalized soil column for the native soils at the site. This soil column was derived from background data and corings performed by the field team. Boring logs included in Appendix F were used to construct the fence diagram (Figure 48).
- 96. Boring logs from water wells drilled for the nearby city of Galena Park, approximately 91 m (100 yd) south of the site, indicate that with depth, shale of either the Beaumont or Lissie Formations becomes predominant. This is consistent with the general Gulf Coast morphology information gathered during the literature search for this area.
- 97. Information from the Gulf Coast Subsidence District and USGS personnel investigating faulting in the region indicate that no faults appear to lie under the site (personal communication, 8 November 1976, Ed Wagoner, General Manager, Galveston, Coastal

Subsidence District). Moreover, the field team saw no signs of seismic activity in the area of the Clinton Disposal Site.

## Pinto Island, Alabama

#### Site description

- 98. The dredged material disposal site on Pinto Island, Alabama (adjacent to Mobile Bay), was selected because it complimented the previously selected locations. It represented an island hydrologic environment, which was subjected to the disposal of estuarine dredged material. Site characteristics are given in Table 10.
- 99. The 26.3 ha (65 acres) Pinto Island site is located west of Mobile, Alabama at the upper terminus of Mobile Bay. A small isthmus at the northern end of the island connects it to Blakeley Island which, in turn, is connected to Mobile. Figure 49 shows Pinto Island in relation to Mobile, as well as the location of Mobile in Alabama.
- 100. The dredged material disposal site at Pinto Island lies in an area which was formerly tidal marshland. The surrounding area on the island exhibits little relief, with the highest point on the island only 4.5 to 6.0 m (15 to 20 ft) above the surrounding waters of Mobile Bay. The rectangular site consists of 26.3 ha (65 acres) of enclosed land which has been used for disposal of dredged material from Mobile Bay (Figure 49). The site is surrounded on three sides by an earthen dike; the natural difference in elevation on the east makes a berm unnecessary in this section. Berm height, as measured on January 17, 1977, was approximately 2.7 m (9 ft) above the level of the dredged material. Dredging at the site during March 1977 made the dredged material nearly level with the dike in most areas.
- 101. Depth of the dredged material as measured by a series of on-site corings on January 17, 1977, ranged from 4.5 to 5.1 m (15 to 17 ft). Figure 50 shows the location of these corings, labeled "monitoring wells".

#### Hydrological features

102. Hydrological investigations at the Pinto Island disposal site were conducted on the days listed in Table 11. Specific

hydrologic tests were performed to complement or substantiate previously gathered background information. Table 11 also summarizes the prominent physical and climatological anomalies observed during each of the visits.

- 103. The results of these investigations were categorized into three subject areas, which, when combined, characterize the hydrological system at the Pinto Island disposal site. They are:
  - a. Climatological environment.
  - b. Surface waters.
  - c. Groundwater characterization

The field testings listed in Table 11 were specifically designed to develop the information required for defining these components.

#### Climatology

104. Historical meteorological data for the Pinto Island dredged material disposal site, based upon a 30-yr average, 1931 to 1960, are tabulated in Table 12. Precipitation, temperature, relative humidity and mean hourly wind speeds were recorded at Bates Field, approximately 24 km (15 mi) west of the site. A more detailed day-by-day record of precipitation and temperature was also collected at Bates Field. This information is included in Appendix G; the dates of field visits are indicated in brackets.

## Surface water

- 105. Surface runoff on Pinto Island drains into Mobile Bay through several drainage ditches; one located west of the site empties into the bay at the southern tip of the island (Figure 50).
- 106. On-site drainage from precipitation and dewatering at the disposal site flows to the eastern portion of the site under normal hydraulic gradient and, subsequently, ponds as observed during the four site visits; ponded water drains through a 0.7 m (2½ ft) pipe at the southeastern corner of the site near the well into Mobile Bay (Figure 50).
- 107. The effect of the tidal fluctuations of Mobile Bay on surface and groundwater gradients at the site were investigated. The mean tidal range of 0.33 to 0.45 m (1.1 to 1.5 ft) in Mobile Bay exerted no measurable influence upon the monitoring wells installed at the site. 15 Water level readings in all the wells

throughout several tidal cycles were measured during field investigations on November 14, 1976, and June 8, 1977; no discernible differences in static water levels were observed during either of these visits, which corresponded roughly to the differences between the summer and winter tidal cycles.

### Groundwater

- 108. Groundwater at the Pinto Island site was characterized through an analysis of the site involving:
  - a. Visual investigation of the surface features.
  - b. Water level readings from the network of well points and monitoring wells.
  - c. On- and off-site pumping tests.
- 109. A visit to the site on January 13, 1977, identified those surface features which could indicate groundwater characteristics. The drainage ditch west of the site was of special interest, since the shallow groundwater emptied into it, demonstrating that the ditch acted as an effluent system. A survey of phreatophytes on-site and adjacent to the fill was also made. The dominant offsite herbs indentified included <u>Pluchea purpurascens</u>, <u>Aster subulatus</u>, and <u>Panicum dichotomiflorum</u>; <u>Phragmites communis</u> was the major on-site species.
- 110. To define groundwater flow patterns, a series of twelve 0.3 cm (1½ in) diameter PVC well points were installed on- and off-site on January 14, 1977. A professional engineering company was subcontracted to survey absolute elevations of these wells to an accuracy of a second-order survey. Bench marks were established on- and off-site for future use. Once the wells were developed and water levels stabilized, static water measurements were recorded from each of the devices, and water level contours developed. Figures 51-54 illustrates the configuration of these contours, which indicate that the groundwater flows roughly in a radial configuration from the site to discharge points in Mobile Bay and the drainage ditch west of the site. Water level elevations, obtained on subsequent field visits to the site, are shown in Figures 51 through 54; as is apparent, basic streamline patterns remained constant.

#### Pumping test

- 111. The third segment of the hydrological investigation was a pumping test designed to provide information concerning the characteristics of the shallow groundwater system. Both on- and off-site pumping tests were originally planned. However, because on-site pumping tests were not successful at the other three sites (due to the properties of the dredged material), no on-site wells were placed at Pinto Island.
- 112. Off-site pumping test and monitoring wells were drilled on August 2, 1977; Figure 50 shows the location of these wells, designated OMW and ONW (off-site monitoring and off-site pumping wells, respectively). Well construction and the lithology in which the well screens were placed are depicted in Figure 55.
- 113. The off-site pumping test was performed on August 2, 1977; results are presented in Figures 56 and 57. A coefficient of transmissibility value of 13.67 1/m/day (11,843 gal/ft/day) was calculated by averaging the results of the pumping and recovery curves. Geology
- 114. Geologic characteristics at the Pinto Island disposal site are presented in terms of both regional and site-specific geology.

## Regional geology

115. The Pinto Island dredged material disposal site is located at the mouth of the Mobile River. Sediments in this part of the Gulf Coast are primarily recent deposits; those in the vicinity of Mobile are Holocene in age. <sup>10</sup> The deposit of these reworked sediments is characteristic of the newly emerging geosynclinal area of the Gulf Coast region. Figure 58 is a portion of a geological map of the area and shows younger sediments characteristic of this portion of the Gulf Coast delta.

## Site geology

116. The geological environment at Pinto Island is identical to that of many of the nearby small sand islands in Mobile Bay. Borings performed to shallow depths, 3.0 m (10 ft) by hand augering, and off-site borings in excess of 6.0 m (20 ft) displayed primarily

sand horizons along with some sandy silts and clays. Figure 59 is a typical soil column developed from the well logs and visual inspection of exposed profiles along the banks of the drainage ditch to the west of the site. On- and off-site borings, recorded during the installation of the monitoring devices are included in Appendix H. These borings provided the subsurface information needed for construction of the fence diagram (Figure 60) which shows the nature of the geologic setting.

- 117. There have been no domestic water wells installed on Pinto Island, and discussion with operators of several industries on the island revealed that no wells have ever been drilled, since the domestic and industrial water supplies are piped from Mobile onto the island.
- 118. Test wells drilled to 15 m (50 ft) for foundation studies for Alabama Dry Docks revealed brackish water in sands and silts with poor water-yielding characteristics (personal communication, 1 August 1977, Henry Seawell, geophysicist, Vester J. Thompson Consulting Engineers, Mobile, Alabama) while well logs from Blakely Island, approximately 1.6 km (1 mile) north of Pinto Island revealed similar sequences of sand, silts and clays.

## Shipping and Sampling Procedures

- 119. The primary goal of this section was to develop a comprehensive sampling and shipping system for dredged material, soil, and water samples so as to obtain representative samples from the field situation. The system had to be designed to prevent contamination from the sampling process itself as well as from chemical and microbiological conversions during the shipping of the samples from the field to the laboratory.
- 120. Pertinent systems were reviewed and evaluated by the project team; basic approaches were adapted to accommodate the variety of site-specific conditions. Soil/dredged material sampling devices, groundwater well installation and sampling methodologies, on-site testing apparatus, as well as sample preservation and shipping techniques were evaluated and adapted to the subject project.

- 121. The literature review assessed methodologies and products in terms of applicability to:
  - a. Dredged material/soil sampling.
  - b. Interstitial and groundwater sampling.
  - <u>c</u>. Soil/dredged material, and groundwater sampling containers.
  - d. Shipping procedures.
  - Ease of well/lysimeter installation, use, and subsequent sampling.
  - $\underline{\mathbf{f}}$ . Adaptability of sampling methods in various environments.
  - g. Reliability of sampling methods.
  - h. Degree of maintenance required after installation.
- 122. Table 13 lists the five general categories for which methodologies were considered and the corresponding potential systems which were evaluated. The consulted references in Table 12 include knowledgeable individuals and reliable literature sources.
- 123. The data were categorized and assessed in terms of the previously-mentioned criteria; the resulting procedures selected are listed in Table 14. As is apparent in the table, existing systems were inadequate for this study. Deficiencies were primarily due to the potential for contamination (i.e., by trace metals) from the use of these devices. Specialized equipment or methodologies were, therefore, developed for the specific demands of the study.
- 124. A brief discussion of the rationale used for the selection of the shipping and sampling procedures listed in Table 14 follows; an explanation of equipment designed for use in those categories where present technologies were inadequate is included.

## Sampling Devices and Procedures

## Dredged material/soil sampling

- 125. The sampling of dredged materials at the four sites as well as of off-site soils at each location consisted of two steps:
  - a. Hand coring to the desired depth.
  - b. Collecting the sample.

Equipment and procedures had to be highly adaptable to a wide

range of site-specific conditions and had to function in materials possessing a wide range of physical properties and compositions.

126. A variety of devices were evaluated as potential methods for coring. Portability and ease of coring were major considerations. Dredged material stability, as well as access into the desired areas at each site, posed major problems for the utilization of heavy equipment, i.e., drilling rigs. The ability to interchange auger heads easily in a variety of dredged material was a major advantage. The bucket and posthold auger heads illustrated in Figure 61 were chosen to provide the widest range of coring capabilities; with extensions to the auger head, it would be possible to core to a depth of over 9.1 m (30 ft).

127. As indicated in Table 14, present techniques for collecting samples were inadequate. A method for collection of the dredged material was, therefore, developed by the SCS project team. The sampler configuration, designed for obtaining both dredged material and soil samples, is illustrated in Figure 62. It consisted of a 0.9 m (3 ft) section of ABS schedule-40 pipe, fitted with a metal trap valve at the bottom (A in Figure 62); the trap valve was coated with 1.5 to 2 mm (0.05 to 0.07 in) of abrasive resistant Teflon (rinsed in ultra-pure distilled water between samplings). The pipe was threaded at the opposite end from the trap valve (Figure 62). By connecting the pipe to 1.5 m (5 ft) plastic extension sections, lower depths could be reached.

128. The coring proceeded with hand augers. When a predetermined depth was reached, the sampler was placed in the hole. The desired dredged material or soil profile was forced into the sample tube by driving the sampler into the material, and the entire assemblage was withdrawn from the cored hole and capped at both ends with ABS-threaded caps (see B in Figure 62). Contacts between the sample tube threads and caps were waxed with melted paraffin to prevent possible leakage. The labeled tube was inserted into a 4 mm polyethylene sheath, further ensuring the integrity of the sample for shipping, and sealed with duct tape at both ends.

129. The sample tube had been appropriately labeled, on the side, listing site designation (code), depth from which the sample

was obtained, and sampling date. Another label defined the relationship of the core to the ground surface, i.e., which end of the sample tube was nearest to the surface.

- 130. The information on the label of the sample tube was recorded on a separate numbered list; the same number was placed upon the sample tube. This list acted as a "back-up" system in the event that the first label on the sample tube was damaged during shipment.
- 131. Deviations from sampling procedures. With only one relatively minor change, the above-mentioned sampling and shipping procedures were used in the field. At Pinto Island, Alabama, the soil and dredged material collection methods designed by SCS were abandoned for a quicker collection approach which did not, however, compromise contamination for expediency; instead of the ABS sampler (Figure 62) employed at the other sites, soil and dredged material were collected with a posthole auger head coated with 1.5 to 2 mil of abrasive-resistant Teflon. The hole was cored to a depth from which a sample was to be taken with a bucket auger head; the head on the auger stem was then replaced with the Telfon-coated posthole auger and the samples collected and placed in a soil tube identical to those previously used. The tube was capped, sealed, and labeled in an identical fashion as on the other three sites.
- 132. The Teflon-coated posthole auger head was used only when a sample was to be obtained, and was rinsed with distilled water between samples. Several additional posthold auger heads were coated and used, when the Teflon coating on the auger head in use indicated that the metal head was soon to be exposed to the soil sample.
- 133. This collection method enabled two team members to collect the soil and dredged material samples, rather than the five or six required for the earlier method. No other segment of the soil/dredged material collection process was altered.
- 134. Field procedures. Specific field procedures were implemented at each of the four case study sites to facilitate sampling and to minimize sample contamination. While most of these field procedures dealt with equipment operations, those developed for

well/lysimeter placements involved more than equipment use.

- 135. Prior to placement of any subsurface sampling device within or outside of the disposal site, a preliminary coring was made near each selected installation area with the hand auger; depths of this coring fluctuated, depending upon the site and whether the hole was within or outside of the disposal area. This preliminary coring provided subsurface data which were useful in determining the exact depth at which each soil/dredged material sample was to be obtained, along with the corresponding placement of the sampling devices. A boring log was kept for each of these initial corings.
- 136. A second coring, to be used for collection of soil samples and sample device placement, was augered within approximately
  1.5 m (5 ft) of the initial hole, to the depth to which soil sample and sampling device placement was to occur, based upon the subsurface data derived from the first coring. This field procedure, while time consuming, ensured that sample collection and sampling equipment installation would be at the optimum subsurface locations. Interstitial and groundwater sampling
- 137. <u>Interstitial water</u>. A variety of devices for the collection of interstitial water was examined; review of the state-of-the-art systems (Table 14) indicated that a pressure vacuum lysimeter was most ideally suited to this task. Therefore, in areas where interstitial water samples were required, the pressure-vacuum soil water lysimeter illustrated in Figure 63 was installed.
- 138. The design for the pressure-vacuum lysimeter is based upon the same principle as that of the porous cup tensiometers routinely used by soil scientists for measuring soil water tension; it is intended to intercept gravitational water percolating through an unsaturated zone prior to reaching the zone of saturation. By placing the lysimeters at various depths in the unsaturated zone, profiles of the water quality can be obtained.
- 139. The lysimeters used for this study are based upon those developed by Parizek and Lane in 1970 at Pennsylvania State University, and consist of a two-bar entry valve porous ceramic cup attached to the end of a 0.9 m (3 ft) long and 4.8 cm (1.9 in) O.D. PVC pipe which is fitted with a rubber stopper at the opposite

end (Figure 63). Two holes are drilled in the stopper to accommodate two 0.6 cm (½ in) 0.D. polyethylene tubes, one for the evacuation and pressurization of the lysimeter and the other for the collection of the water samples. The vacuum or pressure is applied by a hand-operated, two-way pump, resembling a bicycle pump (Figure 64); the portable pump eliminated the need for carrying bulky electrical equipment to each site. During the study, water was pumped to a head of over 6 m (20 ft).

- 140. Two lengths of 0.6 cm ( $\frac{1}{4}$  in) 0.D. ployethylene tubing were inserted into the holes in the rubber stopper attached to one end of the lysimeter, the length of tubing determined by the lysimeter depth in the augered hole. One tube, the vacuum-pressure, extended about 5 cm (2 in) below the stopper, while the other, the discharge tube, extended to within 1.2 cm (0.5 in) of the bottom of the ceramic cup. Prior to the sealing of the top of the lysimeter with paraffin, the discharge tube was coded with strips of identifying tape to distinguish it from the vacuum-pressure tube.
- 141. When more than one lysimeter was installed, bentonite plugs were placed at the top and bottom of the holes and between the lysimeters during backfilling. This helped to eliminate the entry of surface water and to prevent water from channeling to the sampling points by flowing down the polyethylene tubing. The porous ceramic cup in each lysimeter was surrounded by a slurry of wet, fine quartz sand which ensured hydrological continuity with the saturation zone. The final installation for a single lysimeter is depicted in the lower half of Figure 63.
- 142. After placement of the lysimeter, a vacuum was created through the use of the vacuum-pressure pump (Figure 64). One polyethylene tube was crimped by pinch clamp, while a negative pressure of 50 to 85 centibars (15 to 25 in of Hg) was drawn with the hand pump; the other tube was then clamped to maintain the vacuum within the lysimeter. This process is illustrated in Figure 65.
- 143. Water samples were obtained from the pressure-vacuum lysimeter by connecting one polyethylene tube to a collection bottle, and the other tube to the pressure port of the hand pump (Figure 66). The water collected in the lysimeter was forced out of the sampler and into 0.264  $\,$  (1 gal) collection bottle. The water

sample was in turn transferred from the collection bottle into four specially prepared sample bottles which were labeled and chilled prior to shipment in styrofoam containers specially built to minimize microbiological activity. A more detailed discussion of these bottles and shipping procedures is contained in later sections.

- 144. Groundwater. Water samples had to be collected from various levels in the zone of saturation. Existing systems were reviewed (Table 13); PVC tubing threaded to a plastic well point proved the most advantageous. A 3 in. plastic well point, constructed of 40-gauge PVC pipe, was selected for collection of the samples (Figure 67). The well points were slotted with 0.25 mm (0.010 in) openings and threaded at one end.
- 145. Additional lengths of PVC pipe were glued to the well point creating any length desired for well construction. The well point and plastic casing were placed in the sample hole to the required depth. A gravel pack was backfilled the length of the well point to facilitate the movement of water to the well point without clogging. The size of the gravels used for the gravel pack varied, depending upon the subsurface soil conditions. Native soils were compacted over the gravel pack to either the ground surface or to a level at which another well point was to be placed within the same hole.
- 146. Each well point was developed with a hand pitcher pump attached to a length of 1.8 cm (0.75 in) PVC tubing which was inserted, below the water level, into the well. The pump was primed and pumped for 5 to 10 min.
- 147. Water samples were obtained from the well points by lowering a polyethylene tube into the well; one end of this tube was connected to a collection bottle in which a vacuum was applied with the previously mentioned hand pump (Figure 68). When a sufficient amount of water was obtained, it was transferred to four specially prepared sample bottles. By switching the input tubing to the pressure outlet on the pump, pressure was used to transfer the water from the collection bottle into the water sample bottles. The water was forced from the collection bottle through the sampling tube and into a sample container. To minimize the potential of

cross-contamination, the collection bottle and tubing were rinsed with ultra-pure water between sampling.

## Containers for soil, dredged material, and water samples

- 148. The previously described sample tubes were also used as sample containers for the dredged material and soil; sample disturbance was minimized by eliminating the transferring of the samples into a second container. Analytical tests determined both the size and type of water sample bottle to be used. Table 15 lists the bottles selected and their respective sizes.
- 149. University of Southern California personnel determined the appropriate procedures for preparation of containers for water, dredged material, and soil samples (Table 16); the tests to be performed and the elimination of contamination potential were two of the criteria considered.
- 150. As mentioned above, pressure-vacuum lysimeters were selected to sample interstitial waters. Prior to placement in the ground, the lysimeters were cleansed through a series of acid soaks and rinses, described in Table 16 to reduce the contamination potential. Other equipment to reduce contamination is also listed in Table 16. To eliminate cross contamination, the devices used in the collection process for interstitial and groundwater were rinsed between samples; in the field, distilled water was used to rinse the equipment.

#### Shipping procedures

- 151. Shipping containers in which water, dredged material, and soil samples could be packed and transported safely to the University of Southern California were assessed. Review of containers used for past SCS projects involving cross-country sample shipping were studied. The final selections, listed in Table 14 (wooden boxes and plastic ice chests), appeared to provide the best means of protecting the samples during shipment considering the following primary concerns:
  - a. Safety from breakage during handling.
- $\underline{b}$ . Insulative (temperature capacity of containers). Pertinent criteria listed earlier were also considered.
  - 152. Wooden boxes were constructed to accommodate the ABS tube

samples containing both soil and dredged materials. The boxes were made from 1.2 cm (0.5 in) plywood. Five sample tubes along with packed blue ice could be placed in each box. Water sample bottles were shipped in plastic ice chests, packed with either ice or blue ice. Shipping procedures were developed to guarantee that sample shipment was routed in the most expedient manner.

## Sample Preparation

- 153. Upon receipt of dredged material/soil sample tubes, the samples were stored in a constant temperature-humidity environmental chamber at  $4^{\circ}$ C until sample preparation procedures were begun.
- 154. The sample tubes were opened at both ends and immediately emptied into a nitrogen-filled polyethylene bag where they were further purged with nitrogen gas to prevent oxidative processes from occurring. The bagged samples were then placed into a nitrogen-filled glove bag where they could be manipulated with relative ease. Within the glove bag, each sample was mixed and transferred into the following containers:
  - One-litre plastic bottle with cap (for soil mechanics studies).
  - b. Six 20-ml plastic containers with caps (one each for total organic carbon, pesticides, total acidsoluble sulfides, total Kjeldahl nitrogen, total metals, and total phosphorus analyses).
  - One 250-ml polycarbonate centrifuge bottle with cap, 30 g (for water-soluble and ammonium acetate extractable phase).
  - d. One 50-ml tared glass beaker, 10 g (for percent moisture content).
- 155. All transfers were conducted by using plastic or Teflon spatulas; at no time was the sample in contact with glass or metal. The above-listed containers were soaked in 5 percent acid solution for 24 hours then rinsed with double-distilled water before use. The sample containers were appropriately labeled as to site, depth, and experimental purpose and were kept in the environmental chamber. Details of each analysis are given in Appendix L.

156. Attempts to obtain interstitial water from the dredged material and soil samples by means of a hydraulic squeezer and centrifugation at 10,000 rpm for 1 hour were unsuccessful because of the low moisture content of most samples.

## PART III: RESULTS AND DISCUSSION

## Introduction

- 157. The four upland disposal sites chosen for this investigation included freshwater and saline environments. They represented a wide range of physical characteristics. The sizes of the sites varied from 2.4 to 111 hectares (6 to 275 acres). The depths of dredged material ranged from 5 to 35 ft. Native soil varied from sand to clay. The important physical characteristics of the sites are summarized in Table 17. Figure 69 presents the pattern of groundwater interaction with disposal sites.
- 158. Water samples were collected four times during a 9-month period. Sediments were collected during the first and last sampling period. It is imperative to mention here that disposal of dredged slurries occurred intermittently in three of the four monitored sites during the sampling periods.
- 159. It was not possible to collect enough water for all the analyses at all locations. Priorities for analysis were assigned as follows:
  - a. Trace metals.
  - b. Major metal ions.
  - c. Mercury.
  - d. Total organic carbon
  - e. Chloride.
  - f. Alkalinity.
  - g. Sulfate.
  - h. Phosphate.
  - i. Chlorinated pesticides.
  - j. Oil and grease.
- 160. The sediments in the four monitored sites contained a wide range of industrial and domestic pollution. A total of 26 sampling devices were placed in each site. Figure 70 shows the general position of the samplers. Note that the relative depth and distance is not on scale. Twelve of the samplers were placed inside the disposal site, at four locations, three different

depths at each location. Four samplers were placed directly beneath the site at the same four locations. Eight samplers were placed downstream (groundwater flow) from the site, at four locations and two depths. The remaining two samplers were placed upstream (groundwater flow) from the site.

- between the saturated and unsaturated zone, between the new and old dredged material, and also the soil attenuation effect directly below the site. The parameters measured varied among sites as well as within sites. Attempts were made to identify the time-dependent changes in water quality at different depths. Plots of concentrations versus depth, and concentration versus time failed to reveal any systematic changes. For any parameter, both increases and decreases in concentration occurred with time, and random distributions were observed in different locations of the same site. Similar trends were observed in the depth profiles.
- 162. Based on this observation samples collected from the four sampling periods were grouped broadly into:
  - BG: Background samples. Samples collected from the background (upstream) wells.
  - OS: On-site samples. All on-site samples (except those for the Houston site); four locations at three different depths at each site.
  - MW: Monitoring well samples. All off-site (downstream) wells; four locations at two different depths at each site.
- 163. It is extremely difficult to single out a specific trend or mechanism for interpreting the results of this study. Instead, attempts were made to explore the general nature of the systems based on sample variations, i.e., mean and range, pooled from all samples analyzed. As will be explored in later sections, most of the mean values of on-site (OS) group are higher than the monitoring well (MW) and background (BG) group. This could be misleading because of the great variability existing in each site. Student's "t" test will be used to analyze the significance of these differences. The P values obtained are the probabilities of having the difference this large or larger by chance, i.e., lower P values

indicate that the differences are statistically more significant. For samples coming from two different populations, i.e., the two variances cannot be assumed to be equal (as indicated by the F test), the P values will be estimated by the special "t" test as outlined by Davis. 67

- 164. To reflect the groundwater condition, samples were grouped into:
  - a. US: Under-site samples. These included samples collected with the four sampling devices placed directly below the site.
  - <u>b.</u> GW: Groundwater samples from monitoring wells. Samples from the lower depth sampling devices (below groundwater table).
- 165. It was expected that the results would be site-specific since the release and migration of chemical constituents were expected to be affected by the hydrobiogeochemical conditions of the site. A general discussion of the results of the bulk analysis of dredged material/soil from each site, along with the significance of the parameters, is presented in the following section. Possible mechanisms regulating the transport of trace contaminants are briefly reviewed. The chemical properties of the water samples and the migration trends of the contaminants, with emphasis on groundwater quality, are also discussed in detail.

## Characteristics of Dredged Material/Soil

#### Particle size distribution

- 166. The results of the particle size distribution analysis are given in Appendix I, Tables II to I4. The classification of sediment texture was based on the Corps of Engineers, "Triangular Classification Chart" shown in Figure 71.
- 167. Particle size distribution is an important property associated with confined disposal operations. Coarse-grained dredged material tends to settle rapidly within the site. Finer particles tend to be carried with the effluent to the receiving waters due to insufficient residence time or turbulence. A decrease in the relative sand portion in the effluent compared with influent was reported by Hoeppel et al. <sup>68</sup> and Lu et al. <sup>69</sup>. This will, of course, be a function of the original sediment characteristics,

size of site, and rate of dredged material disposal. Consequently, it is generally expected that the dredged material that settles in land disposal sites will be more sandy than the original bottom sediments. A horizontal stratification may also exist with finer particles settling more closely to the effluent weir. In this study, all but one sample contained more than 50 percent sand, with many made up of more than 90 percent sand.

- 168. Sayreville samples collected for this study were more varied than the Pinto Island samples. Textures ranged from sand to clay sand. The clay content averaged 20 percent for the on-site samples, and 24 percent for the native soil away from the site; both are the highest among the four sites.
- 169. The Houston site is an isolated aquifer system, separated from the regional aquifer by underlying native clay. All samples were collected within the site. A wide range in particle size distribution was observed (Table I3).
- 170. The Grand Haven on-site samples were not as uniform as the samples from the other three sites. Two of the on-site locations (MA and MB), which were much more clayey than the other two (MF and MG), were closer to the effluent weir. Two of the off-site samples showed that the top few feet of the surrounding soil is clay or silty sand followed in sequence by a layer of sand and clay, a typical aquifer profile.
- 171. Particle size distribution has a profound effect on the chemical properties of leachates produced. Finer particles provide a larger surface area per unit weight for sorption and exchange reactions. It is well-known that clay particles have a higher cation exchange capacity and a higher affinity for organic matter, trace metals, pesticides, and nutrients. In general, the finer soil textures provided for greater attenuation of trace contaminants. Moisture equivalent, bulk

## density, hydraulic conductivity

172. The moisture equivalent reported in Tables II to I4 was determined in accordance with ASTM Designation D 425-69, "Standard Method of Test for Centrifuge Moisture Equivalent of Soils." It should be noted that this procedure only approximates natural per-

colation, and it cannot be assumed that the centrifuge moisture equivalent represents the in situ field capacity. Any investigators have shown, however, that the moisture equivalent can be corrected with the actual field capacity for many soils.

- 173. The field capacity is defined as the smallest value to which the water content of a soil can be reduced by gravity. The Sayreville site had the highest mean moisture equivalent followed by the Grand Haven, Houston, and Pinto Island sites (Table 17). This parallels the trend based on the relative clay contents.
- 174. Except for the Sayreville samples, most samples had moisture contents close to or exceeding the moisture equivalent values, suggesting a groundwater recharge situation. The conclusion was reinforced by field observations. At the time of sample collection, the surface of the Sayreville site was dry and cracked. Snow covered the Grand Haven site, a potential recharging condition. Four inches of rain was recorded at Pinto Island during the 2 weeks preceding the sampling. Part of the site was actually ponded. Light drizzle was reported at the Houston site. The moisture content was close to the moisture equivalent in the Houston site.
- 175. The bulk density (apparent density) is defined as the weight per unit volume of a material, including voids inherent in the material as tested. This is an important parameter because the void spaces are the pathways in which the solute will travel. The result of the bulk density analysis are given in Table II to I4.
- 176. Hydraulic conductivity is another parameter that may influence the flux of leachates. Hydraulic conductivity, also called the coefficient of permeability, has the unit of velocity, cm/sec, and reflects the rate of water flow. The significance of this lies in the fact that slow flow rates through the dredged material or soil provide longer reaction times for the interactions of solvent contaminants and the dredged material/soil particles.
- 177. The laboratory measured values, obtained using the falling head method, are reported in Tables II to I4; the statistical analysis is given in Table 19. A wide range of values covering five orders of magnitude was observed. This is another indication of the heterogeneity of the sites.

## Cation exchange capacity

178. Ion exchange is a reversible chemical reaction that takes place between ions in a solution in contact with ions held near a mineral surface. The total capacity of the mineral to exchange cations is defined as the cation exchange capacity (CEC), and is usually expressed in meq/100 g dry weight soil.

179. Malcolm and Kennedy  $^{75}$  attribute the range of CEC in soils to: (a) parental material (geology), (b) age of weathering surface, (c) climatic factors, (d) degree of weathering, and (e) completeness of chemical and physical dispersion. In simpler terms, the CEC is related to soil texture, type of clay mineral, organic matter content, pH, and the solid to solute ratio.  $^{74-76}$ 

180. Exchange is found to take place faster in fine sediments, and fine sediments have a relatively high CEC. Carroll  $^{74}$  reported that, due to the difference in structure and chemical composition, clay minerals have exchange capacity ranges (in meq/100 g) in the order of halloysite ( 2 to 10) < kaolinite ( 3 to 15) < glauconite (11 to 20) < attapulgite (20 to 30) < illite (10 to 140) < montmorillonite (70 to 100) < vermiculite (100 to 150). The order of replaceability of the common ions found in clay minerals has been found to be:  $^{73}$ 

 $Li^{+} < Na^{+} < K^{+} < Rb^{+} < Cs^{+}$  and  $Mg^{++} < Ca^{++} < Sr^{++} < Ba^{++}$ .

181. Malcolm and Kennedy<sup>75</sup> reported a study that demonstrates the significant contribution of organic matter to the CEC of certain size fractions of sediments. The CEC of sand and gravel fractions were found to range from 7 to 16 meq/100 g; 17.6 meq/100 g for the fine silt fraction, and 53.6 meq/100 g for the fine clay fraction. Except for the silt fraction, after accounting for the organic matter, the CEC of the mineral portion was relatively constant at 5.5 to 8.0 meg/100 g.

182. Toth and Ott $^{76}$  reported that the organic matter content of bottom sediments is responsible for about 80 percent of the CEC. Their findings on river sediments, bay sediments, and freshwater impoundment sediments indicate that CEC values, which ranged from 7 to 100 meq/100 g, were much higher than thoseof soil, which ranged from 1 to 15 meq/100 g. They also reported that the order

of abundance of three exchangeable trace metals in the sediments was  ${\rm Zn} > {\rm Cu} > {\rm Ni}$ . The quantity of exchangeable trace metals was highly correlated with the amount of organic matter present.

183. On studying the concentration of five elements in suspended materials in streams, Turekian and Scott<sup>77</sup> reported that, although the CEC of the total suspended load was higher for the Mississippi River and rivers to its west than those to the east, the concentrations of the elements were considerably lower and the composition resembled that of shale. They concluded that the difference was not due to the CEC but rather due to a greater amount of a mobile trace metal-rich soil component and to higher industrial discharge in the eastern rivers.

184. In this study, a wide range of cation exchange capacities was found (Table 19). In general, the mean values are expected to reflect relative texture of the samples. As stated before, Pinto Island samples were generally the most sandy, and they also had the lowest CEC, an average of 11 meq/100 g. The highest CEC was 51 meq/100 g. That particular sample contained 14 percent clay, more than most of the samples from the Pinto Island site.

185. Sayreville samples had the highest mean CEC of 55 meq/100 g and also the highest average clay content. Samples from Grand Haven and Houstonwere intermediate, again showing the relations between CEC and particle size distribution. However, linear regression analysis showed that only Sayreville samples exhibited a high correlation between CEC and clay content (R = 0.78). This is probably due to the difference in TOC content and the difference in clay mineralogy.

### pH and Eh

186. pH and Eh are very important factors in regulating the direction and extent of reactions in dredged material and soil. Eh is a measure of the availability of electrons or the electrochemical potential of the system (corrected on the hydrogen electrode). Oxidation and reduction reactions are defined as reactions that involve loss or gain of electrons. In general, oxidation should result in low pH values, and low pH values favor the migration of most trace elements. Redox reactions are

energy-requiring systems. In natural systems, the energy usually comes from the decomposition of organic materials. To complete the reaction, some substances must act as electron acceptors. The electron acceptors that exist in disposed dredged material include oxygen, nitrate, Mn(IV) oxides, Fe(III) oxides/hydroxide, sulfate, and carbon dioxide. The above are listed in order of their oxidizing potential. Reduction of carbon dioxide to methane, the last in the sequence, seldom occurs because most of the organic matter will be oxidized by the other acceptors listed.

188. The biological activities result in a changing supply of 78-82 organic matter. Total redox equilibrium is not found in nature. Therefore, the Eh measurements lack specific thermodynamic meaning. They only represent a gross sum of all the simultaneous redox pair reactions. However, Eh measurements will serve the function of indicating the general redox condition of the systems.

189. Patrick and Mahapatra classified soil (adjusted to a pH of 7) into four categories:  $^{86}$ 

- a. Oxidized soil: Eh > +400 mV.
- b. Moderately oxidized soil: +400 to +100 mV.
- c. Reduced soil: +100 to -100 mV
- d. Highly reduced soil: -100mV to -300mV

190. Pearsvall and Mortimer <sup>87</sup> reported that products of oxidation (ferric, nitrate, sulfate) were found in soil, mud, and water with an Eh (at pH of 5) of +350 mV and that their reduced counterparts (ferrous, ammonia, sulfide) were present in zones below this value. They suggested that the mechanisms regulating redox potential in all three types of systems are similar in nature.

191. As a rough guide to the progress of reduction,
Ponnamperuma 88 compiled a list of critical potentials observed from stirred soil suspensions:

Observation	Eh (at pH of 7), mV
Oxygen (undetectable)	+330
Nitrate (undetectable)	+220
Manganese (detectable)	+200
Iron (detectable)	+120
Sulfate (undetectable)	-150

192. For this study, the Eh and pH were measured by carefully sticking a platinum and glass electrode into freshly exposed dredged material or soil. The results are presented in Tables I5 to I8. The Pinto Island pH ranged from 4.2 to 7.6, with most values close to 7. The on-site dredged material was slightly more acidic than the off-site soil (means of 6.5 and 7.0, respectively). The Eh ranged from -232 to +353 mV for the dredged material and -82 to +368 mV for the soils. Similar ranges of results were found for other sites.

193. The wide range of Eh and the relatively small range of pH measured were expected. Similar results for various sediments and soils have been extensively reported in the literature. 5,87,89-92 Eh and pH are theoretically related:

Eh = E<sub>0</sub> = 
$$\frac{0.059}{n}$$
 log  $\frac{O_x}{Red}$  - 0.059  $\frac{m}{n}$  pH

where  $\begin{bmatrix} O_{\mathbf{X}} \end{bmatrix}$  = activity of oxidized species  $\begin{bmatrix} \operatorname{Red} \end{bmatrix}$  = activity of reduced species  $\begin{bmatrix} \operatorname{n} \end{bmatrix}$  = number of electrons involved  $\begin{bmatrix} \operatorname{m} \end{bmatrix}$  = number of protons involved

194. As mentioned before, Eh is expected to be related to the organic matter present. High TOC usually signifies low Eh levels. However, the Eh, pH, and TOC data indicate that this relationship does not always hold true.

195. During dredging operations, the sediment is mixed with the overlying oxygen-rich water. It is possible that the sediment-bound biostimulants will be affected and transformed. Upon disposal, some organic matter will be oxidized by biological activities. The Eh and pH should often show localized variations within site sediments, depending on the nature and amount of the organic matter present (e.g., its biological activities), oxygen diffusion rate, 93,94 and the sediment buffering capacity. Eh and pH are the major variables that dictate the extent of most reactions. It was not surprising to find highly localized distribution of soluble species in this study.

## Organic matter and other gross parameters

- 196. The main component of organic matter in sediments is usually humus, resulting mainly from the biodecomposition of lignins, cellulose, and proteins. 93,94 Humus is primarily composed of highly insoluble complex macromolecules, and is believed to be firmly adsorbed onto clay minerals. 95,96 Metal ions can form strong ionic or covalent bonds with humus by means of different functional groups (e.g., carbonyl, hydroxyl, amide and sulfhydryl bonding). These mechanisms appear to be partially responsible for the migration and accumulation of trace metals in soils and marine sediments.
- 197. Nutrients can be released from the biodegradation of organic matter in the dredged material. Due to its complexity, it is impossible to determine the exact nature of the organic matter. A few general parameters were used to characterize its gross properties.
- 198. Total organic carbon. The average onsite dredged material TOC value ranged from a low of 0.27 percent for the Houston site to a high of 3.8 percent for the Grand Haven site. The Sayreville offsite soil TOC was slightly higher than the on-site dredged material (1.9 percent and 1.4 percent respectively). Both Pinto Island and Grand Haven had higher on-site values than the off-site values (0.97 percent and 0.53 percent for the Pinto Island site, 3.8 percent and 2.5 percent for the Grand Haven site).
- 199. Total organic carbon (TOC) in dredged material probably originates from the sedimentation of biological detritus. Few soluble organic compounds found in natural waters are thermodynamically stable. Decomposition of organic matter depletes the dissolved oxygen and reduces the Eh. In addition to its high cation exchange capacity, the organic matter in soil also possesses a high capacity to form insoluble complexes with metal ions. Therefore, high TOC in the sediment usually signifies a potential for the immobilization of trace metals through organic matter binding.
- 200. <u>Nitrogen compounds</u>. Ammonia and organic nitrogen are other nutrients which were measured in this study. The principal form of nitrogen added to sediments is organic nitrogen, with the bulk usually present as biologically protected protein frag-

ments. Ammonia is most often formed from the decomposition of protein (deamination) by saprophytic bacteria:  $^{102}$ 

## Bacteria

Protein (Organic N)——Ammonia

This process is known to take place with or without oxygen, but is much faster under aerobic conditions because the more active aerobic bacteria decompose organic matter at an accelerated rate. However, net release of ammonia is greater in anaerobic conditions due to slower biological uptake. Ammonia thus tends to accumulate under anaerobic conditions. Accumulation of ammonia in anaerobic lake sediments was observed by Austin and Lee 103 and high ammonia content in deep sea interstitial waters was reported in several studies. 104, 105

201. When oxygen is present, ammonia is further converted into nitrite and nitrate , mainly by aerobic nitrifying bacteria. The dominant pathway is as follows:  $^{102}$ 

$$\begin{array}{ccc}
 & \text{Nitrosomonas} & \text{Nitrobacter} \\
 & \text{NH}_3 & \longrightarrow & \text{NO}_2 & \longrightarrow & \text{NO}_3
\end{array}$$

- 202. The TKN data are given in Appendix H. The statistics are summarized in Table 19. The average on-site value ranged from a low of 269 mg/kg for the Pinto Island samples to a high of 3170 mg/kg for the Sayreville samples. While there is little leaching of organic nitrogen, dredged material may serve as a nitrogen source for groundwater because of the soluble end-products (ammonia or nitrate) resulting from the biological activities.
- 203. Phosphorus compounds. Phosphorus exists in sediment and soil in the inorganic and organic form, and in valence state from +5 to -3. The main transformation of phosphorus is the release and mobility of the orthophosphate ion. Chang and Jackson 106 classified the inorganic phosphate in the soil into four main groups: calcium phosphate, aluminum phosphate, iron phosphate, and reductant-soluble phosphate, extractable after the removal of the first three forms. The possibility of the formation of aluminum phosphate minerals (wavellite and variscite) and iron minerals (vivianite and dufrenite) in acid soils has been demonstrated by Stelly and Pierre.

mainly as apatite, anapaite, and bushite.  $^{78,108}$ 

204. The total phosphorus data are given in Tables I5 to I8. Dredged material from the Grand Haven site had a high total phosphorus content (average of 1700 mg/kg) followed by Sayreville (1490 mg/kg), Pinto Island (1360 mg/kg) and Houston (1280 mg/kg). The Sayreville soil samples were as high as the dredged material (Table 19). Pinto Island and Grand Haven soil samples contained considerably less total phosphorus.

205. The transformation of the stable solids is greatly affected by Eh and pH. Phosphate associates mainly with iron and aluminum in acid soils and sediments; calcium phosphate is predominant in neutral and alkaline soils. The importance of this in regulating phosphate transport will be explored in greater detail when discussing the results of the soluble phosphate in leachates.

206. Oil and Grease. The average oil and grease content at the Sayreville site was higher in the surrounding soil than in the on-site sediments, even though on-site averages are higher than those at the Pinto Island and Grand Haven sites. This is similar to the relative distribution of TOC in these sites. The exact reason for this cannot be assessed by this study. The Sayreville site is bordered by two heavily used highways. It is possible that the exhaust and emission from automobiles may have contributed to the observed result. An oil and grease extract can include a great variety of organic compounds besides petroleum derivatives. Materials which are extractable with petroleum ether include glycerides, high molecular weight fatty acids, gasoline, oils, waxes and other hydrocarbons. Petroleum compounds constitute the greatest proportion in sediments from industrialized areas. High oil and grease in the sediment thus usually indicates industrial pollution. 109 However, there is essentially no information available on the relationship between such residues and degradation of water quality. 109,110 The average oil and grease value for each site is given in Table 19.

207. <u>Sulfides</u>. The acid-soluble sulfide measured in this study included hydrogen sulfide and certain metallic sulfides. The

main source of sulfide in sediment interstitial waters is dissolved sulfate. Thermodynamic calculations indicate that sulfate is unstable in the presence of abundant organic matter and absence of oxygen. However, the reduction of sulfate to sulfide in natural systems is known to occur only through biological mediation. The bacteria that carry out this reaction are grouped together under the common name "sulfate reducers." The most widely distributed species belong to the Desulfovibrio genus. Their metabolic activities have profound consequences. The end result of the reduction reaction, as illustrated by the following general equation, include metal sulfide precipitation, increase in alkalinity, carbonate precipitation, Eh and pH modification:

$$2 \text{ CH}_2\text{O} + \text{SO}_4^- \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O} + \text{CO}_2$$
 $\text{Ca}^{++} + 2 \text{ HCO}_3^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3$ 
 $\text{M}^{++} + \text{S}^- \rightarrow \text{MS}$ 

208. The production of  $CO_2$  can lower the pH, and the free sulfide produced will combine with the available metallic ion  $(M^{++})$  to form stable solids.

209. Acid-soluble sulfide was detected in all samples. The value generally correlated with the ToC and Eh. The highest value was 2357 mg/kg, found in an off-site Sayreville sample. That sample also had a relatively high ToC (1.7 percent) and low Eh (-168 mV). The lowest value from that site was 23 mg/kg, with a ToC value of 0.02 percent and an Eh value of 408 mV.

210. The availability (or mobility) of trace metals in soil were usually directly related to the solubility products of the metallic sulfides.  $^{118}\,$ 

Mn > Fe > Zn > Ni > Cd > Pb > Cu > Hg

The existence of sulfide in the dredged material/soil samples indicated that sulfides could be the controlling solids for most trace metals. Due to the low solubility of metallic sulfides, the metals are expected to be immobilized. 118

## Chlorinated hydrocarbons

- 211. The chlorinated hydrocarbons measured include three forms of PCB's (Aroclor 1242, 1254, 1260) chlorinated pesticides: op' and pp' isomers of DDT and its analogs DDE and DDD; and dieldrin. Attempts were made to determine the concentrations in the soluble and solid phases. After forty filtered samples from different sites and depths showed no detectable soluble species, no further analyses were made on water samples.
- 212. Adsorption onto clay and organic matter may explain the fact that no soluble species were detected in this study. Chlorinated hydrocarbons are very hydrophobic. They tend to come out of solution easily and be adsorbed to solid surfaces available to them. Most chlorinated hydrocarbons in the environment are adsorbed onto the soil and sediment particles. The transport of these species is regulated to a large extent by adsorption and transport with clay and organic matter. Leland et al. 123 reported that the chlorinated hydrocarbons were mostly concentrated in the upper 2 cm of the sediment. The clay-sized fraction has been shown to be able to adsorb muchgreater amounts of chlorinated hydrocarbons than sand because finer fractions usually contain both higher organic content and a larger surface area.
- 213. The complete results for the dredged material/soil samples are presented in Table J1 to J5; ranges, means, and standard deviations are given in Table 20. Most samples contained all the species studied. Total DDT ranged from below the detection limit to 850 ppb. The major form was op' and pp' DDE. A similar distribution in sediments was reported by Choi and Chen. 119 Average total DDT (Table 20) was highest for the Sayreville site (96 ppb) followed by Pinto Island (78 ppb), Houston (67 ppb) and Grand Haven (44 ppb). Average total PCB's ranged from a high of 0.58 ppm for the Sayreville site to a low of 0.14 ppm for the Grand Haven site. Average dieldrin was found to be highest at Sayreville (2.3 ppb) followed by Grand Haven (1.2 ppb) and Houston and Pinto Island (both averaged 0.8 ppb) (Table 20).
- 214. The average total PCB values correlated very well with the average total DDT values (R = 0.70). Total PCB's correlate

fairly well with the percent clay content (R = 0.44). It was generally expected that soil TOC would correlate with the chlorinated hydrocarbons. This was not observed in this study.

215. In general, the dredged material contained higher chlorinated hydrocarbon levels than the off-site soil samples. special trend was found for the distribution of the species in the on-site dredged material. For the off-site soil samples, concentrations of all species decreased with depth. This was observed in Pinto Island, Sayreville, and Grand Haven. For the Houston site, all samples collected were on-site dredged material, and no special trend was found. Since no soluble species were detected, it is concluded that chlorinated hydrocarbons will not leach out from dredged material disposal sites.

# Trace metal analysis

- 216. Soil and dredged material samples were analyzed for trace metals in the soluble fraction, the exchangeable fraction, and the gross concentrations. This analysis was performed sequentially by shaking with water then ammonium acetate, and by digestion with strong acids. The detailed results are given in Table J5 to J8. Attempts to squeeze out interstitial water from these samples failed because of low moisture content.
- 217. In general, for each sample, iron was highest in the total analysis followed by the major ions, Na, K, Mg, and Ca. The concentrations of metals followed roughly the order:

 $Mn > Zn > Cu > Pb > Ni > Hg \approx Cd$ 

218. In the soluble and exchangeable fractions, no particular concentration trends were found other than for manganese. major ions in the soluble phase generally ranked:

Na > K > Mg > Ca > Fe > Mn

in the soluble phase and

Ca > Mg > Na > K > Mn

in the exchangeable phase.

219. No apparent relations were found in these soil analyses and the subsequent analyses of water samples. This result is not surprising since bulk analysis is not a good indicator for potential availability. Depending upon the chemical phase of the

species, metals may be totally unavailable (e.g., they may exist in the crystal structure of the soil particles) or readily available (in solution or adsorbed onto the particles).

220. Also, the results confirmed the highly dynamic, complex nature of the soil-dredged material system. The samples excavated from the sites may not represent the actual site conditions after elapsed time.

# Characteristics of Leachates/Interstitial Waters General considerations

- 221. The composition of the dredged material and interstitial water (leachate) at a disposal site is highly dependent on the dredging and disposal practice. The ambient water quality and the sediment characteristics play an important role because the dredged slurry is mainly composed of the water overlying the dredging site sediments. The sediment-water ratio and time of contact affect the exchange of chemical species.  $^{125-130}$  Variation of sediment interstitial water composition with depth has been extensively reported.  $^{131-135}$  Thus, depth of dredging is also an important factor.
- 222. Chemical constituents usually are enriched in the interstitial waters of sediments. 135-138 Concentration gradients with depth have been observed, and the diffusion of ions along the gradient has been suggested as one of the mechanisms for the transport of the ions. 139-142 After dredging and disposal, this stratification is disrupted. Instead, an uneven distribution of high constituent concentrations could develop in the disposal site.
- 223. The size of the site and the quantity and frequency of dredgingalso affect the fate of pollutants. Recent reports on the influent/effluent studies of certain upland dredged material disposal sites have shown that larger ponded sites generally retain more polluted sediments. This characteristic is the result of the site providing longer settling times for removal of the finer particles. It is well-known that small particles have greater affinities for trace metals and organic

matter. 2,69,144,145

- 224. Another factor that influences the leachate composition is the repeated drying and wetting of site sediments due to evaporation, drainage, and precipitation. <sup>146</sup> In a literature review <sup>110</sup> it was shown that drying of taconite tailings prior to a leaching test caused a release of copper from the tailings which did not occur if the tailings were maintained in their wet conditions prior to the leaching test.
- 225. Merz and Stone 147 pointed out that solid waste disposal sites are usually aerobic near the surface and become more anaerobic towards the bottom. However, within unsaturated zones, traces of oxygen are often present so that zones or pockets of anaerobic and aerobic decomposition may exist side by side at any depth.
- 226. Lu<sup>94</sup> and Lu and Chen<sup>148</sup> reported that sulfide is usually the controlling solid for most metals in the reducing environment and and that oxides and hydroxides are the controlling solids in the oxidizing environment. The solubility of oxides and hydroxides is in general much higher than that of their sulfide counterparts. Thus, the oxidizing forms of most metals are generally more mobile than their reduced forms.

## Factors affecting the migration

### of constituents through dredged material and soil

- 227. If there were no attenuation or enrichment mechanisms, contaminants could tend to percolate from sediments under varying environmental conditions and eventually end up in the sea or remain totally unavailable. However, soil is a highly complex, dynamic system. Recent studies on leachates from sanitary landfills indicate that, due to certain properties of the soil, transport of contaminants can be retarded. Nonuniform environments in the ground can develop pockets of varying constituent mobilities. 149-152
- 228. Soil and dredged material have very similar characteristics. The following is a list of factors that would affect the migration of constituents in soil and dredged material: 153-156
  - a. Soil texture.
  - b. pH.
  - c. Oxidation-reduction.

- d. Dilution.
- e. Ion exchange.
- f. Adsorption.
- g. Solubility/complexation.
- h. Diffusion.
- i. Biological effects.
- 229. Soil texture. The importance of soil texture, pH, Eh, and ion exchange was discussed in the previous section. Soil texture may play a governing role in the migration of trace contaminants. Many attenuation mechanisms involve solid surfaces. The finer the particle, the greater the available surface, and the greater the potential for attenuation by these mechanisms. Water flow may also be retarded in areas possessing high clay contents, thereby allowing greater reaction time between the soluble and solid phases.
- 230. Redox and pH. pH affects the stability of solid minerals and precipitates. Changes in redox conditions may change the controlling solids. In general, oxidation results in low pH, and reduction increases pH values. Migration of trace contaminants is usually favored in low-pH environments.
- 231. Dilution is a simple mechanism. Dilution can occur either from percolation of surface drainage and precipitation or from the contaminant reaching the groundwater table. This is the only important mechanism for the attenuation of chloride ions. 83,157 Dilution also plays an important role in regulating other major ion concentrations, especially sodium and potassium.
- 232. <u>Sorption</u>. Adsorption is a very important mechanism for the removal of many soluble metals. Krauskopf<sup>158</sup> proposed that this is the possible control mechanism for regulating concentrations of Zn, Cu, Pb, Cd, Hg, Ag, and Mo in seawater. Clays, soil organic matter, and iron and manganese oxides and hydroxides are excellent adsorbents for many trace constituents. 158-162
- 233. Organic matter and clay minerals account for most of the ion exchange character of soils. Both ion exchange and adsorption are surface phenomena. Very often, it is impossible to distinguish between the two types of reactions. Ion exchange reactions are

governed by the law of mass action. Since the trace metals such as Cu and Cd are much lower in concentration than the major ions such as  $\text{Ca}^{++}$  and  $\text{Na}^+$ , it is generally assumed that ion exchange is more important for major ions; however, adsorption and exchange reactions may also be important in regulating trace metal concentrations.

- 234. Solubility and complexation. The solubility effect governs each soluble species through its solubility constant. If the solubility of the species exceeds the solubility produce,  $K_{\rm sp}$ , precipitation will tend to occur. This may be important for Ca<sup>++</sup> and  $Mg^{++}$ .
- 235. For most trace metals, it is necessary to consider the complexation effect in addition to the solubility calculation. Most trace metals are known to exist in various complexes with soluble inorganic and organic ligands. In general, complexation increases the soluble metal concentration. However, soil organic matter also has a great affinity for forming complexes with trace metals. In the latter case, trace metals will be immobilized. The solubility and complexation effects can be expressed by the equations below.
- 236. The concentration of metal ions as governed by the solubility of the solid  ${\rm M}_{\rm p}{\rm X}_{\rm q}$  is given by

$$\begin{bmatrix} M_f \end{bmatrix} = \begin{pmatrix} \frac{(K_{sp})M_pX_q}{\gamma_M^p & \gamma_N^q & X_f \end{bmatrix}^{1/2} \\ \text{where } \begin{bmatrix} M_f \end{bmatrix} = \text{concentration of free metal ions} \\ \begin{bmatrix} X_f \end{bmatrix} = \text{concentration of free anions} \\ \gamma = \text{ion activity coefficient} \\ K_{sp} = \text{solubility product} \\ p, q = \text{positive integers} \end{bmatrix}$$

237. Due to the complexation effect, the concentration of the complexed species is given by

$$\begin{bmatrix} M_{m} L(i)_{n} \end{bmatrix} = M\beta(i)_{nm} \begin{bmatrix} M_{f} \end{bmatrix}^{m} \begin{bmatrix} L(i)_{f} \end{bmatrix}^{n} \frac{\gamma_{M}^{m} \gamma_{L}^{n}(i)}{\gamma_{M}^{m}L(i)_{n}}$$

The total metal concentration can then be derived from

$$\begin{bmatrix} M_{t} \end{bmatrix} = \begin{bmatrix} M_{f} \end{bmatrix} + m \sum_{n=1}^{k} \sum_{i=1}^{\Sigma} \begin{bmatrix} M_{m}L(i)_{n} \end{bmatrix}$$

$$= \begin{bmatrix} M_{f} \end{bmatrix} + m \sum_{n=1}^{k} \sum_{i=1}^{\Sigma} \beta (i)_{nm} \begin{bmatrix} M_{f} \end{bmatrix}^{m} \begin{bmatrix} L(i)_{f} \end{bmatrix}^{n} \frac{\gamma_{M}^{m} \gamma_{L(i)}^{n}}{\gamma_{M}L(i)_{n}}$$

where  $M_{+}$  = total metal concentration

i = ligand species

j = total number of ligands

 $L(i)_f$  = free concentration of  $i^{th}$  ligand

 $n, m = composition of the complex M_mL(i)_n$ 

 $K = Number of ligands (li) coordinated with <math>M_n$ 

 $\beta(i)_{nm}^{}$  overall formation constant of complex  $M_mL(i)_n$ 

- 238. <u>Biological effects</u>. Biological activities may promote a change of pH (e.g., production of CO<sub>2</sub>), change in redox condition (e.g., reduction of sulfate to sulfide), mineralizing of trace metals and nutrients, and modification of organic matter. In short, all of the previous mechanisms discussed can be affected.
- 239. Diffusion is the net movement of soluble species from a region of high to one of low concentration. This is known to be a very slow process, 142 but could be an important mechanism if the flow rate is small.

# Migration of Contaminants and Nutrients in Confined Land Disposal Areas

240. The concentration of constituents in leachate/interstitial water is highly influenced by the factors discussed in the previous section. Soil and dredged material have very similar characteristics. Factors that cause attenuation in one system may

have neutral or even opposite effect in other systems. Because of this, concentration profiles are seldom homogeneous, and the profiles will be different for different elements.

241. A discussion of the results based on each individual parameter is presented in this section. The relative concentration of the on-site leachate and off-site interstitial water was established for each parameter through a statistical analysis of variance. This helps to identify the pollution potential of the parameters. The extent of contamination will be discussed by comparing the background groundwater samples, groundwater directly below the site, and groundwater in the vicinity of the disposal site (off-site monitoring stations).

#### Total dissolved solids

- 242. Theoretically, since every solution exists in an electrically neutral state, the sum of the cations (positively charged ions) expressed in meq/100 g should be balanced by the sum of the anions (negatively charged ions) expressed in the same unit. In this study, the major cations measured were sodium, potassium, calcium and magnesium; the major anions analyzed were chloride, sulfate, and alkalinity. The total concentrations (sum of anions and cations) ranged from a few to about 600 meg/1. Figure 72 shows the relationship between the cations and anions and the total cation concentration. Assuming the above ions constitute the bulk of the charge balance, the difference between the cations and anions was below 10 percent of the total cation concentration in most samples. This is an acceptable experimental error considering that, besides analytical error, some ions such as NH<sub>A</sub> and NO<sub>3</sub> were not measured. These ions have been shown to exist in concentrations as high as a few hundred mg/l in various interstitial waters 88,105 and in groundwater.87
- 243. The major ions also contribute the bulk of total dissolved solids (TDS), the concentrations of which are shown in Table 21. Table 22 sums up the averages of the major ions from each site. Among the sites, the on-site samples closely reflect the salinity of the dredged area. A comparison of the three averages for each site shows that the off-site samples were lower

than the on-site samples but the background samples were lowest of the three. This suggests an increase of TDS caused by leaching from the site. This will be explored further in the discussion of each individual parameter.

#### Chloride

- 244. The on-site chloride concentration ranged from an average of 167 mg/l for the Grand Haven site to 8333 mg/l for the Sayreville site, typical values for freshwater and brackish water systems. Both the Pinto Island and Sayreville sites showed significantly higher concentrations for the on-site samples (Table 22), indicating the salinity level of the overlying water of the dredging site. The Houston samples had concentrations between those of the above two sites. For the Grand Haven site, due to the relatively wide spread of concentration, the differences between the two sets of samples are not statistically significant (P = 0.65), i.e., there is a 65 percent chance that the two sets of samples will have similar chloride concentrations.
- 245. The observed ranking among the sites was expected. The dredged material disposed of at the Sayreville, Houston, and Pinto Island sites was from estuarine environments. The dredged material was thus expected to have a higher chloride content than the offsite soil samples. Grand Haven is in the Great Lakes area. Both the dredged material and the surrounding soils are in a freshwater environment. The differences in chloride concentration, if there were any, should therefore have been small.
- 246. The on-site Sayreville samples exhibited a general pattern showing an initial decrease then increase in concentration with time. About 14.5 in. of precipitation in the area was recorded for the 3 months between the first and the second sampling periods. The dilution effect of the rainfall probably accounts for the relatively low chloride concentration obtained for the second set of samples (Table K2). The sharp increase for the third set was no doubt due to dredging activities that started immediately before the sampling period.
- 247. Similar trends were observed for the Pinto Island site. It is interesting to note that the samples obtained after dredging

(second set) were actually lower than the ones obtained before dredging. Again, this could be due to a dilution effect from precipitation. More than 3 in. of rain fell in the 3-week period before the second sampling date. Another possible explanation is the location of dredging. As discussed before, predredging water quality is very important when considering the on-site interstitial water characteristics. If the dredging occurred farther upstream from the channel, i.e., farther away from the brackish water compared to the last dredging site, the salinity should decrease.

248. The groundwater chloride concentrations are summarized in Table 23. The general pattern for the chloride concentration was low levels in the background (BG) samples, peaking in samples under the site (US), then decreasing as the groundwater migrated to the monitoring wells (GW).

249. This pattern is supported by the statistics given in Table 23. Considering all the factors previously discussed, dilution is the only plausible attenuation mechanism affecting the migration of chloride ions. 153,157 It is reasonable to propose that chloride leached into the groundwater table below the sites during leachate migration through the unsaturated zone. It was subsequently diluted by mixing with less saline groundwater. The monitoring well samples were higher in chloride than the background but lower than the samples from under the site. This shows chloride was also migrating laterally from the site. Pinto Island provides the best evidence for this as the monitoring well groundwater was shown to be consistently higher in chloride content than the interstitial water a few feet above it (Table K4).

250. At the Sayreville site, the average values also had a ranking similar to the Pinto Island samples, i.e., groundwater samples under the site were higher than the downstream monitoring samples which in turn were higher than the background groundwater samples. However, in the monitoring well locations, some of the soil interstitial waters were shown to have higher chloride than the groundwater samples directly below them. This is in contrast to the trend observed in the Pinto Island site. Thus it appears that the

lateral migration is not as obvious in Sayreville. Yet, a reconnaissance survey indicated that the monitoring wells were inundated by the 1.5 m (5 ft) tidal range of the Raritan River. This probably disrupted the levels separating groundwater and interstitial water. Chloride retained in the upper locations may be further concentrated through evaporation.

251. In conclusion, dredged material in the Pinto Island and Sayreville sites contained higher soluble chloride than the natural surroundings of the disposal sites. Chloride was observed to leach from the sites, and migrate away from the sites. In the Grand Haven site, no chloride leaching was observed. This is probably due to the fact that both the dredged material and the disposal site are in a freshwater system.

Sodium and potassium

252. Sodium and potassium have very similar chemical properties. A linear regression analysis on their means reaffirmed that the two metal ions were highly correlated (R = 0.84). The highest sodium concentration was found in the Sayreville site and averaged 4310 mg/l. The next highest mean value was 2690 mg/l for the Houston site. Pinto Island, with an average of 1485 mg/l, ranked next. Grand Haven, being in a freshwater environment, ranked last with an average of 110 mg/l. This reflected the salinity of the dredged material.

253. Both sodium and potassium are known to form very soluble compounds. The solid forms that exist in the natural environments are mostly complex primary and secondary minerals such as K-feldspars, K-micas, Na-feldspars, and Na-montmorillonite. The dissolution of these minerals usually leads to the formation of another mineral, i.e., incongruent dissolution, and the dissolution rates are also very slow. Thus, dissolution/precipitation reactions are expected to have an insignificant effect on the migration of sodium and potassium.

254. As indicated by the low P values, both sodium and potassium were higher in the on-site samples than in the off-site samples (Table 22), suggesting a leaching potential. Neither sodium nor potassium is regarded as a hazardous contaminant in

low concentrations. However, high levels can make drinking water unpalatable, limit the use of water for agriculture, and promote degradation of the structure of aerable soils. The transport of these two ions serves as an indicator of the rate of leachate migration. It has been reported that suspended clay minerals, after being transported by river to the marine environment, exchange magnesium and sodium for calcium and potassium. 161,162 The evidence provided in these studies was an increase in Na to K and Ca++ to Mg++ ratios. Both Pinto Island and Sayreville dredged material samples had higher interstitial water salinities than the surrounding native soil. The raio of Na to K was indeed found to be higher for the on-site than the off-site samples (31.2 and 11.7 for Pinto Island, 28.6 and 16.8 for Sayreville). The ratios in the exchangeable phase were found to be 2.0 and 0.33 for Pinto Island and 2.9 and 1.3 for Sayreville. Therefore, exchange between sodium and potassim may affect the migration of these two ions. However, it was expected that, in comparison to dilution effects, exchange mechanisms would only play a minor role at these two sites. This is especially true for the freshwater Grand Haven site, where the average ratio of Na to K was very similar for the on-site and the off-site samples. Again, this is probably due to the relatively low salinity concentrations in all samples.

255. The concentration pattern at Houston was quite varied. Certain spots would show an increase in concentration with time or depth, while an opposite trend would be found at another spot. In short, the pattern was very random. This was probably a result of ion exchange and the repeated drying and wetting due to precipitation and evaporation (resulting in downward salt movement with the gravitational water and upward movement with the capillary water).

256. Based on the samples analyzed, it is concluded that sodium behavior was similar to that of potassium and chloride. Dredged material contained higher soluble sodium and potassium than the off-site monitoring samples, thus establishing a leaching potential. Both ions were observed to leach from the sites. Possible mechan-

isms controlling the migration of these two ions included dilution and ion exchange with dilution the dominant mechanism. Calcium and magnesium

257. The averages and ranges for the calcium concentrations are given in Table 22. For the on-site samples, Houston had the highest average concentration (428 ppm), followed in order by Sayreville (386 ppm), Grand Haven (356 ppm), and Pinto Island (140 ppm). For the Pinto Island and Sayreville disposal sites, values of off-site samples were only about half of those of on-site samples. The averages for the on- and off-site Grand Haven samples were quite close: 356 ppm and 321 ppm, respectively. Student's "t" test results suggested that the differences were significant for the Sayreville and Pinto Island sites (p < 0.01). For the Grand Haven site, a p value of 0.35 was obtained, meaning that there was a 65 percent chance that the on-site samples were higher than the off-site samples. Since on-site samples were higher, there was a potential for calcium to migrate away from the sites.

258. A comparison of the samples underneath the site with the off-site monitoring well and background samples indicated that the under-site samples were statistically higher than the other two groups, suggesting either a calcium leaching front or dissolution of calcium solids underneath the disposal sites. In the Grand Haven site, the monitoring well samples were higher than the samples beneath the site (Table 22). This result was probably due to dissolution of calcium carbonate.

259. Concentrations of magnesium correlate fairly well with calcium. The level of magnesium was found to be higher in the on-site than the off-site samples from Pinto Island, Sayreville, and Grand Haven, suggesting a leaching potential. Comparing the averages among the sites indicates that the magnesium concentration followed the order of seawater > brackish water > freshwater. The average seawater magnesium concentration has been reported to be 1296 mg/1, and the average river water concentration has been reported to be 9 mg/1. The Sayreville site, which had highest relative sediment interstitial water salinity values, also showed the highest average magnesium concentration of 728 mg/1.

Houston, next in relative salinity, had the second highest average, 394 mg/l; Pinto Island, a low-salinity site, had an average of 174 mg/l; and Grand Haven, a freshwater site, had an average of 71 mg/l.

- 260. Possible mechanisms controlling the transport of calcium and magnesium included dilution, precipitation/dissolution, and ion exchange. Comparing the results with those for K, Na, and Cl, it is evident that dilution cannot solely account for the observed results. Drever 163 considered several clay mineral transformations and syntheses as mechanisms for the removal of mangesium in the ocean. Possible reactions included:
  - a. Transformation involving major changes in the clay lattice, such as the conversion of kaolinite to chlorite:

$$Al_2Si_2O_5(OH)_4 + SiO_2 + 5 Mg^{+2} + 7H_2O$$
  
=  $Mg_5Al_2Si_3O_{10}(OH)_8 + 10H^+$ .

- b. Transformation involving only the interlayer positions such as "upgrading the degraded lattices," i.e., restoring ions lost due to weathering.
- c. Synthesis of other clay minerals.

However, these reactions were expected to play an unimportant role in the present study due to the very lengthy time frame involved in most clay mineral transformations.

261. The transport of magnesium was probably regulated by the solubility of simple solids such as brucite  $({\rm Mg(OH)}_2)$ , magnesite  $({\rm MgCO}_3)$ , nesquehonite  $({\rm MgCO}_3 \cdot 3{\rm H}_2{\rm O})$ , hydromagnesite  $({\rm Mg}_4\,({\rm CO}_3)_3\,({\rm OH})_2\,3{\rm H}_2{\rm O})$ , and dolomite  $({\rm CaMg}\,({\rm CO}_3)_2)$ . An activity ratio diagram for the hydroxide and carbonate solids is shown in Figure 73. At pH < 7.2, nesquehonite  $({\rm K}_{\rm Sp}=10^{-5\cdot 4})$  is expected to be the controlling solid. From pH 7.2 to 9.7 hydromagnesite  $({\rm K}_{\rm Sp}=10^{-29\cdot 5})$  will be the controlling solid. At pH 9.7 and above brucite  $({\rm K}_{\rm Sp}=10^{-11\cdot 6})$  becomes the stable solid. Most analyzed samples were below pH 8. Thus, the solubilities of nesquehonite and hydromagnesite may regulate most of the magnesium mobility and transport.

262. Calcium is known to form stable carbonate and sulfate solids

in sediments. The solubility constants for the two common solids are:

Calcite 
$$CaCO_3 = K_{sp} = 10^{-8 \cdot 3}$$

Gypsum  $CaSO_4 = K_{sp} = 10^{-4 \cdot 6}$ 

Many of the Sayreville samples had very low pH (3 to 5), with low carbonate and high sulfate concentrations (7 x  $10^{-3}$ M). It is possible that calcium sulfate was the major controlling solid for the concentrations in many Sayreville samples, while calcium carbonate was the controlling solid for other samples. Figure 74 is an activity ratio diagram for the two solids. It was constructed assuming  $C_t = 10^{-2.5}$ M and  $SO_4 = 10^{-2.5}$ M. It is seen that calcium sulfate only becomes the controlling solid when pH is below 3.5. The following tabulation is a compilation of the observed calcium ranges and the predicted concentrations, assuming that calcium carbonate solubility is the controlling mechanism:

	Observ	red (mg/1)	Predicted		
Sayreville	50 to	620	200	to 2000	
Pinto Island	25 to	440	20	to 2000	
Houston	205 to	1020	20	to 2000	
Grand Haven	80 to	610	20	to 2000	

The observed data were within the range calculated from the calcite solubility, suggesting that this was the major controlling mechanism.

263. One other possible mechanism affecting the migration of calcium is ion exchange with magnesium. As previously discussed for the Pinto Island and Sayreville sites, interstitial water and dredged material samples contained much higher calcium concentrations than the off-site samples. As the leachate percolated away from the site, magnesium may have exchanged with the calcium ions held by soil particles:

$$Mg^{+2}$$
 + Soil - Ca =  $Ca^{+2}$  + Soil -  $Mg$ 

The average  ${\rm Mg}^{+2}/{\rm Ca}^{+2}$  ratio changed from 1.25 for the on-site Pinto Island samples to 0.53 for the off-site samples. The change in the  ${\rm Mg}^{+2}/{\rm Ca}^{+2}$  ratio between seawater and river water had been suggested

as evidence for the preferential ion exchange reaction between the two ions. The exchange effect ( ${\rm Mg}^{+2}/{\rm Ca}^{+2}$  ratio) is not as evident in the other sites. The reason for this is not known.

- 264. In conclusion, it appeared that soluble calcium was higher in the on-site dredged material samples than the off-site soil samples for the Sayreville and Pinto Island sites. The migration is controlled by ion exchange and the dissolution of calcite if pH is greater than 3.5; gypsum if pH is less than 3.5. Based on the samples analyzed, calcium appeared to have leached from the Pinto Island and Sayreville sites.
- 265. Soluble magnesium concentration was shown to be higher in the on-site samples than the off-site samples (true in three case study sites) i.e., a leaching potential was established. Actual leaching of magnesium was observed in three sites. This was indicated by comparing the groundwater samples below the sites with the groundwater samples downstream from the sites and samples upstream from the sites. Possible mechanisms controlling the migration of magnesium included dissolution of magnesium solids such as nesquehonite and hydromagnesite and ion exchange. Alkalinity and TOC
- 266. A wide range of alkalinity was registered in this study. Among the monitored sites, the average alkalinity value was in decreasing order, Houston (1092 mg/l), Grand Haven (589 mg/l), Pinto Island (446 mg/l), and Sayreville (196 mg/l). For individual samples, the values ranged from nil to close to 2000 mg/l.
- 267. Many of the samples with negligible alkalinity were from the Sayreville site. Alkalinity is a measure of the acid neutralization capacity and is determined by titration with acid down to a pH of 4.3 to 4.5. Many of the Sayreville off-site and background samples had pH levels below 5. This accounts for the low alkalinity values for that site.
- 268. Alkalinity was found to be higher in on-site samples than off-site samples from the Pinto Island and Grand Haven sites (Table 22), suggesting a leaching potential for these two sites. A comparison of the samples collected beneath the two sites with back-

ground and off-site samples, showed that for both the Pinto Island and the Grand Haven sites, the average values were in decreasing order; under-site, off-site monitoring well, and background. This suggests that an alkalinity leaching front had arrived at the under-site locations and was diluted as it traveled downstream (groundwater) away from the site. By comparing the on-site and off-site monitoring well samples, an attenuation of 48 percent (from 446 to 230 mg/l) was registered at the Pinto Island site, and an attenuation of 45 percent (from 589 to 326 mg/l) was obtained at the Grand Haven site.

269. In most natural waters, alkalinity is due mainly to carbonate and bicarbonate ions and is defined as:

Alk = 
$$\left[\text{HCO}_{3}^{-}\right]$$
 + 2  $\left[\text{CO}_{3}^{-}\right]$  +  $\left[\text{OH}^{-}\right]$  -  $\left[\text{H}^{+}\right]$ 

As will be discussed in the later sections, the carbonate concentration is very important because carbonate solids are believed to be the controlling solids for most metals in an oxidizing environment.

270. Mechanisms controlling the levels and transport of alkalinity include dissolution of carbonate solids, weathering reactions, and oxidation-reduction reactions. Weathering reactions were probably too slow to explain the findings in this study. Dissolution of solids such as calcite and hydromagnesite was expected to play an important role and this will be discussed in later sections.

271. Biological activities also play a dominant role. The oxidation of organic matter during sulfate reduction changes alkalinity levels:

$$2 \text{ CH}_2\text{O} + \text{SO}_4 \longrightarrow \text{H}_2\text{S} + 2\text{HCO}_3$$

Brooks, Presley, and Kaplan postulated that in marine sediments this is followed by another reaction:  $^{114}$ 

$$Ca^{+2} + HCO_3^- = CaCO_3 + H^+$$

This controls the calcium concentration and buffers the pH.

- 272. In this study, TOC appeared to be highly correlated with alkalinity among the sites (R = 0.86), another indication that biological action might affect alkalinity. Like alkalinity, TOC was potentially leachable from the Pinto Island and Grand Haven sites (Table 22). For these two sites, the samples collected from underneath the sites were higher in TOC than the off-site monitoring well samples, which in turn were higher than the background samples. This trend was similar to that of alkalinity. A TOC attenuation of 27 percent was noted for the Pinto Island site, and a 63 percent attenuation was observed at the Grand Haven site.
- 273. For the Sayreville site, the TOC level was higher in the off-site than the on-site samples. This is probably due to the fact that the off-site area is in part a salt marsh. The decay of vegetation serves as the source for the TOC. It is well known that organic matter forms stable complexes with many trace metals. The high TOC content may in part account for the higher trace metal levels in many off-site samples at Sayreville. The oxidation of organic matter by sulfate, as previously discussed, may also explain the relatively low pH found in the vicinity sediments. Low pH also favors the dissolution of most trace metals.
- 274. To sum up, alkalinity and TOC were observed to be higher in the on-site than the off-site Pinto Island and Grand Haven samples. Both were shown to have leached to the groundwater below the sites. The transport of alkalinity is probably regulated by dissolution of calcite and biological oxidation. For the Sayreville site both soluble TOC and alkalinity were higher in the off-site soil samples than the on-site dredged material samples. The reason for this is not clear. It may be due to the decay of vegetation since the vicinity of the site was formerly a salt marsh. Phosphate
- 275. The distribution of phosphate is dependent on a highly complex and dynamic system. In a literature review, Patrick and Mahapatra cited that phosphate availability under submerged conditions was governed mainly by the form and solubility of iron phosphate compounds. In a reducing environment, iron is converted from the ferric to the ferrous state, and phosphate is released.

If aluminum abounds, phosphate will be reprecipitated as aluminum phosphate. The phosphate levels detected in this study were fairly low, ranging from below the detection limit to a high of 0.91 ppm. There was no apparent correlation between the soluble phosphate and total phosphate concentrations. Only the Pinto Island site showed a higher on-site average than the off-site average (0.1 to 0.03 ppm, respectively).

276. Stumm and Leckie plotted the phosphate solubility of various solids versus pH. 165 The following is a summary of the phosphate concentration based on ferric phosphate (dufrenite) and calcium phosphate (apatite) solubility:

рн	Ferric-PO <sub>4</sub>	Apatite-PO <sub>4</sub>
3	$10^{-3\cdot 4} \text{ M} = 12 \text{ ppm}$	-
4	$10^{-5}$ M = 0.31 ppm	
5	$10^{-5\cdot 2} M = 0.20 ppm$	<u>-</u>
6	$10^{-5}$ M = 0.31 ppm	
7		$10^{-5\cdot 4}$ M = 0.12 ppm
8		$10^{-7 \cdot 2} M = 0.002 ppm$

277. At low pH, the predicted value is much higher than the observed values. Sayreville background samples were very acidic, with pH ranging from 2.8 to 7.2. Soluble phosphate ranged from 0 to 0.11 ppm. The highest soluble phosphate concentration was in a sample which had the highest pH (7.2). This was probably due to less phosphate adsorption by clay minerals, since phosphate adsorption is favored by low pH. At other pH values, the predicted concentrations of ferric iron phosphate and calcium phosphate together with adsorption onto clay minerals may have accounted for the phosphate content detected.

278. In conclusion, soluble phosphate was at very low levels. Only the Pinto Island site showed a leaching potential (0.1 ppm on-site versus 0.03 ppm off-site). Actual leaching was not observed. Phosphate can be ruled out as a potential water quality problem.

#### Trace metals

- 279. With the exception of iron and manganese, concentrations of trace metals in the leachate samples were mostly in the ppb or sub ppb range. At such low concentrations, precipitation/dissolution, complexation, and adsorption are expected to play dominant roles in regulating their transport.
- 280. In general, in an aerobic environment, the stable solids that control the solubilities of these metals are oxides, hydroxides, or carbonates. Under reducing conditions, most trace metals may gradually precipitate as sulfides due to the generally much lower solubilities of these sulfides.
- 281. Acid-soluble sulfide was detected in all of the dredged material and soil samples. However, although hydrogen sulfide could be smelled in a few of the water samples during sampling, no free sulfide was detected in the water samples. The threshold of smell for hydrogen sulfide may be as low as 10<sup>-9</sup> moles/1, or a few ppb. 78 It is possible that hydrogen sulfide did exist in the samples but was below the detection limits for the methods used (electrode and methylene blue photometric method).
- 282. The low sulfide concentrations could have resulted from either of two methods. The first possibility is that the free sulfide was oxidized by oxygen which diffused into the samples during collection. Water samples were collected either from well points or suction lysimeters. It is highly probable that traces of oxygen could have diffused into the water inside the sampling devices. Attempts to improve this condition by flushing the samples with nitrogen were dropped because of the inaccessibilities of the sampling locations and the difficulties in carrying the nitrogen tanks.
- 283. The second possibility is that the sulfide concentrations were below the detection limits for the methods used. Although large amounts of free sulfide ( $\rm H_2S+HS^-+S^=$ ) could be produced from the reduction of sulfate by organic matter, the concentration remaining in solution might be small due to the formation of metallic sulfides, mainly FeS and FeS<sub>2</sub>.
  - 284. Both possibilities are equally probable. The metal sul-

fide solubilities are orders of magnitude lower than those for metal carbonates, hydroxides, or oxides. Although existing in undetectable concentrations, sulfide could still play a governing role at extremely low concentrations. The following calculation, based on the solubility products of cadmium, illustrates the importance of sulfides.

285. The solubility product for CdS is  $10^{-26.96}$  and Cd CO $_3$  is  $10^{-13.69}$ . The ratio of the sulfide ion concentration and carbonate ion concentration is given by:

$$R = \frac{\left[s^{=}\right]}{\left[co_{3}\right]} = \frac{(K_{sp}) \ cds}{(K_{sp}) \ cdco_{3}} = \frac{10^{-26.96}}{10^{-13.69}} = 10^{-13.27}$$

286. If R is greater than  $10^{-13.27}$ , CdS becomes the controlling solid, and vice versa. The carbonate concentration is usually about  $10^{-5}$  to  $10^{-7}$ M. Therefore, if S is greater than  $10^{-20.27}$  to  $10^{-18.27}$ M, CdS will be the controlling solid for cadmium.

287. Obviously, it is not yet possible to detect sulfide at such low concentrations. However, we can estimate the conditions under which sulfide solids become important. Consider the following equations:

$$1/8 \text{ SO}_4^{2-} + 5/4 \text{ H}^+ + e^- = 1/8 \text{H}_2 \text{S}_{aq} + \frac{1}{2} \text{H}_2 \text{O}_{aq} - \frac{\log K^*}{5.12}$$

$$1/8 \text{H}_2 \text{S} \text{(aq)} = 1/8 \text{Hs}^- + 1/8 \text{H}^+ -0.88$$

$$1/8 \text{Hs}^- = 1/8 \text{S}^- + \frac{1}{8} \text{H}^+ -1.75$$

Combining the three equations gives:

$$1/8 \text{ SO}_{4}^{2-} + \text{H}^{+} + \text{e}^{-} = 1/8 \text{ S}^{=} + \frac{1}{2} \text{ H}_{2}^{O}$$

$$2.49$$

$$Eh^{O} = 2.303 \frac{\text{rt}}{\text{n}} \log K = 0.059 \log K =$$

$$= 0.147 \text{ V at } 25^{O}\text{C}$$

$$Eh = Eh^{O} + 0.059 \log \left[\frac{\text{SO}_{4}^{=}}{\text{S}^{-}}\right]^{1/8} - 0.059 \text{ pH}$$

$$S^{=} \frac{1}{8}$$

<sup>\*</sup> K's obtained from ref. 78 and 118.

287. In this study the sulfate ion concentration ranged from  $10^{-1.6}$  to  $10^{-3.2}$  and most pH values were within the range of 5 to 8. This makes the second term to the right of the equation roughly equal -0.306 to -0.496 and

$$Eh = -0.160 \text{ to } -0.350 + 0.007 \text{ ps}^{=}$$

$$where ps^{=} = -\log \left[ s^{=} \right]$$

$$Eh = redox \text{ potential in Volts}$$

$$For Cd, CdS \text{ becomes dominant when } \left[ s^{=} \right] \text{ is greater than } 10^{-20.27}$$

$$or ps^{=} = 20.27$$

$$Eh = -0.160 \text{ to } -0.350 + 0.007 \text{ X (+20.27)}$$

$$= -0.018 \text{ to } -0.208$$

288. Choosing the upper limit, cadmium in any sample with Eh below -18mV may be controlled by the solubility of CdS. Stumm and Morgan estimated that for samples that give a sulfide odor, the partial pressure of  $\rm H_2S$  is between  $10^{-2}$  to  $10^{-8}$  atm. or the hydrogen sulfide ( $\rm H_2S$ ) concentration is around  $10^{-3}$  to  $10^{-9}\rm M$ . For samples with Eh below - 18mV and pH = 5, hydrogen sulfide is given by

$$\begin{bmatrix} H_2 S \end{bmatrix} = \underbrace{\begin{bmatrix} H^+ \end{bmatrix}^2 \begin{bmatrix} S^- \end{bmatrix}}_{K_1 \quad K_2}$$

$$K_1 = 10^{-7}$$

$$K_2' = 10^{-14}$$

$$= \frac{(10^{-5})^2 \quad (10^{-20 \cdot 27})}{10^{-21}}$$

$$= 10^{-9 \cdot 27} \approx S_t$$

The value is very close to that estimated by Stumm and Morgan,  $^{78}$  and is a plausible value because only some samples had a  $\rm H_2S$  smell.

289. In an oxidizing environment, most trace metals could be controlled by the solubility of the metal carbonate solid:

$$MCO_3 = M^{+2} + CO_3$$

The free metal concentration is given by:

$$M^{+2} = \frac{K_{sp}}{\left[CO_3^{-1}\right]}$$

$$pM = pK_{sp} + log C_{t} + log \alpha_{2}$$

where  $C_{+} = \text{total}$  carbonate concentration

$$= \left[ H_{2} co_{3} \right] + \left[ Hco_{3}^{-} \right] + \left[ co_{3}^{-} \right]$$

$$\alpha_{2} = \frac{H^{+2}}{K_{1} K_{2}} + \frac{H^{+2}}{K_{2}} + 1^{-1}$$

 $\rm K_1$ ,  $\rm K_2$  = first and second dissociation constants of  $\rm H_2CO_3$ ,  $10^{-63}$  and  $10^{-10.3}$ , respectively.

290. No direct measurement of  $C_{\rm t}$  was performed. However, total carbonate concentration can be estimated from alkalinity and total inorganic carbon data. At  $\rm K_1$  < pH <  $\rm K_2$ ,  $\rm C_t$  is roughly equal to alkalinity since the majority of the carbonate species exist as bicarbonate ions. At lower pH values, especially when alkalinity approaches 0, the carbonic acid ( $\rm H_2CO_3$ ) concentration is expected to increase. TIC measures at low pH values ranged from below the detection limit (5 mg/l) to 20 mg/l. It is reasonable to assume  $\rm C_t$  ranged from  $\rm 10^{-3.5}$  moles to  $\rm 10^{-1.5}$  moles, with most samples in the neighborhood of  $\rm 10^{-2}$  moles (corresponds to 500 mg/l alkalinity).

291. Based on  $C_{\rm t}$  and the previously derived equation derived before, the range of free metal concentrations can then be estimated. Using the  $K_{\rm sp}$  listed in Table 24 and assuming  $C_{\rm t}=10^{-3.5}$  and  $10^{-1.5}$  moles, the free metal concentration expected in this study is given by:

 $_{p}Cd^{+2} = 10.1 \text{ or } 12.1 + \log \alpha_{2}$ 

$$_{p}^{cu^{+2}} = 6 \text{ or } 8 + \log \alpha 2$$
 $_{p}^{Fe^{+2}} = 6.9 \text{ or } 8.9 + \log \alpha 2$ 
 $_{p}^{Mn^{+2}} = 5.7 \text{ or } 7.7 + \log \alpha 2$ 
 $_{p}^{Ni^{+2}} = 4.7 \text{ or } 6.7 + \log \alpha 2$ 
 $_{p}^{Pb^{+2}} = 9.8 \text{ or } 11.8 + \log \alpha 2$ 
 $_{p}^{Zn^{+2}} = 7.2 \text{ or } 9.2 + \log \alpha 2$ 

Figures 75 and 76 are graphic presentations of the expected metal ranges using pH as the master variable. The diagrams are constructed by assuming:

$$\frac{\text{dlog}_2}{\text{dpH}} = 0 \text{ at } pH > pK_2$$

$$= 1 \text{ at } pK_1 < pH < pK_2$$

$$= 2 \text{ at } pH < pK_1$$

#### Cadmium

among all metals analyzed. The on-site water samples averaged 0.8 ppb for the Grand Haven site to a high of 58 ppb for the Sayreville site. The highest concentration was 200 ppb in a Sayreville leachate. Many of the Sayreville samples were in the 100-ppb range. Samples from other sites were relatively uniform, and were in the low or sub-ppb range. The spread for these samples was so small that a difference of 0.6 ppb between the on- and off-site Grand Haven samples was shown to be statistically significant. In this case, the off-site average was higher than that of the on-site water samples (Table 22).

293. Considering the groundwater conditions (Table 23), the Grand Haven site background and monitoring well waters had slightly higher concentrations than the water samples obtained directly beneath the disposal area (averages of 1.4 and 0.92 ppb compared

to 0.79 ppb). For the Pinto Island samples, one high concentration (46 ppb) was detected in a second set under-site sample. The rest were all about 1 ppb. Hem<sup>170</sup> reported that the median concentration of cadmium in 726 samples of water taken from rivers and lakes of the United States was a little below 1 ppb. The low concentration range found in the Grand Haven and Pinto Island samples indicates that cadmium would pose no potential threat to deterioration of the groundwater quality.

294. The highest cadmium concentrations were found in the Sayreville samples. One of the monitoring wells (NJF 2) had a concentration of about 100 ppb throughout the study (Table K2). The two background wells (NJI and NJJ) also showed consistently high values. The local groundwater flow was a radial pattern flowing away from the site (Figure 69). It was difficult to select a good background well to reflect the impact of the leaching of cadmium from dredged material. The distribution of cadmium was probably regulated by the local environmental conditions, especially the Eh and pH.

295. Krauskopf<sup>158</sup> calculated that seawater is undersaturated with respect to cadmium. He suggested that precipitation as cadmium sulfide is a possible control mechanism in some localized reducing environments where the free sulfide concentrations are high. As discussed above, cadmium sulfide precipitation probably occurred if the Eh values were below -18 mV. The following tabulation shows the range of cadmium concentrations observed in samples with Eh above -18 mV and samples with Eh below -18 mV:

Site	Samples Below -18 mV	Samples Above -18 mV
Sayreville	1 to 8 ppb	1 to 204 ppb
Pinto Island	1.2 to 4 ppb	<1 to 46 ppb
Grand Haven	< 1 ppb	<1 to 4 ppb
Houston	1 to 102 ppb	1 to 8 ppb

It appears that soluble phase cadmium was higher under more oxidizing conditions (above -18 mV) where cadmium carbonate is the controlling solid.  $^{167,168}$  The cadmium concentration is given by:

$$cd^{+2} = \frac{K_{sp}}{[co_3^{=}]} = \frac{10^{-13 \cdot 69}}{[co_3^{=}]}$$

296. In the reducing environment, where cadmium sulfide is the stable solid, cadmium concentration is given by:

$$cd^{+2} = \frac{K_{sp}}{[s^{=}]} = \frac{10^{-26.96}}{[s^{=}]}$$

Depending on the sulfide concentration, cadmium can exist in the range from the high ppb level to ten orders of magnitude lower.

297. Cadmium is known to form stable soluble complexes with various ligands, and Lu and Chen, 148 suggested that chloride is the most important ligand in seawater. The total cadmium concentration measured would be:

$$cd_{t} = cd_{f} \left\{ 1 + B_{1} (c1^{-}) + B_{2} (c1^{-})^{2} + B_{3} (c1^{-})^{3} + B_{4} (c1^{-})^{4} + B_{5} (c1^{-})^{5} + B_{6} (c1^{-})^{6} \right\}$$

Where 
$$Cd_f = \frac{K_{sp}Cds}{(s^{=})}$$
 in the reducing environment

and = 
$$\frac{K_{sp}^{CdCO_3}}{(CO_3^{=})}$$
 in the oxidizing environment

298. As discussed previously, cadmium sulfide probably becomes dominant when  $pS^{2-}$  is smaller than 20, or  $pS_t$  is smaller than 9. Figure 77 is a distribution diagram of the sulfide species assuming  $pS_t = 9$ . Referring to Figures 75 and 77, the free cadmium concentration range, under either sulfide or carbonate solids control, is calculated for each site to be as follows:

Site	pH Range	CdS Control	CdCO <sub>3</sub> Control			
Sayreville	3 to 7	4.5 X 10 <sup>-4</sup> to 1.8 X 10 <sup>3</sup> ppb	0.7 ppb to 1.1 X 10 <sup>4</sup> ppm			
Pinto Island	4.8 to 8.2	1.8 X 10 <sup>-5</sup> to 3.5 ppb	1.1 ppb to 7.1 X 10 <sup>2</sup> ppm			
Grand Haven	5.8 to 7.7	3.5 X 10 <sup>-5</sup> to 0.06 ppb	7.1 ppb to 4.5 ppm			
Houston	5.4 to 7.8	3.5 X 10 <sup>-5</sup> to 0.28 ppb	5.6 ppb to 35 ppm			

- 299. In an oxidizing environment the predicted values were close to the observed values for samples with high pH. The reverse was true for the reducing environment where the predicted values ranged from 0.06 to 3.5 ppb for samples having pH values from 3 to 5.8. At the other end of the pH scale the observed values were several orders of magnitude lower than the theoretical values.
- 300. Jenne<sup>159</sup> proposed that cadmium coprecipitates with iron and manganese when the latter two are oxidized. Adsorption on clay minerals and organic matter may be another immobilizing mechanism. It was suggested that in soils, clay minerals and organic matter are the major components involved in adsorptive reactions. <sup>171,172</sup> Both mechanisms are likely to reduce the cadmium concentration in an oxidizing environment.
- 301. In summary, there was a potential for cadmium to leach from the Pinto Island and the Sayreville site. However, no actual leaching was observed. It appeared that cadmium transport was regulated to a great extent by the controlling solids and by adsorption onto clay minerals. The average cadmium concentration was very low. It is concluded that soluble cadmium from diked dredged material disposal practice poses no threat to groundwater quality. Copper
- 302. A wide range of copper concentrations was found at the Sayreville site. The on-site water samples ranged from 3 ppb to 3 ppm and averaged 231 ppb. The four monitoring wells, which were located from a few to about 100 m away from the site, provided water samples with a slightly higher average concentration of 500 ppb and a wider range (1 ppb to 6.1 ppm). The two background wells were located about 700 m (NJI) and 1500 m (NJJ) away from the Sayreville site. Both background wells had relatively high copper concentra-

tions. The copper concentration of these two wells averaged 2.6 ppm during the 9-month study.

303. Many of the groundwater samples at Sayreville had copper in the ppm range. The highest value, 11.4 ppm, was found for a background well sample (NJJ). The highest concentration in a monitoring well sample was 6.1 ppm, found in NJF. The highest undersite sample was only 2 ppm, found in NJD. All these values were from the third set of samples, which were collected after new disposal activities had resumed at this site. One month later, NJJ and NJF samples decreased to 330 and 492 ppb, repsectively. No sample was collected from NJD during that period.

304. Due to the high concentrations found in the background and monitoring wells, it was not possible to assess the copper leaching potential at this site. As discussed before, the ground-water pattern of the Sayreville site is a complex radial flow system. This makes it very difficult to locate a true background well. Locations too close to the site might be already affected by the leachates. Locations too far away from the site might be influenced by pollution sources other than the dredged material disposal site. For example, the National Lead Industries, which manufactures many inorganic and organic chemicals, discharges its industrial waste in the vicinity. The impact of this on the local groundwater quality is not known.

305. The locations with high copper levels (NJJ, NJI, and NJF) had very low pH values (3 to 4) and high Eh. It has been suggested that in the oxidizing environment soluble copper is probably regulated by carbonate hydroxyl solids such as malachite (Cu $_2$  CO $_3$  (OH) $_2$ ). The other important copper solids include copper hydroxide (Cu(OH) $_2$ ) and copper carbonate (CuCO $_3$ ). At pH 3, the ion ratio is given by the following equations:

$$R_{1} = \frac{K_{sp} Cu (OH)_{2}}{K_{sp} \left[Cu_{2} CO_{3} (OH)_{2}\right]^{\frac{1}{2}}} = 10^{-2 \cdot 7} = \frac{\left[OH^{-}\right]}{\left[CO_{3}^{-}\right]^{\frac{1}{2}}} = \frac{10^{-11}}{\left[CO_{3}^{-}\right]^{\frac{1}{2}}}$$

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$$R_{2} = \frac{\kappa_{sp} \text{ Cuco}_{3}}{\kappa_{sp} \left[\text{ Cuco}_{3} \text{ (OH)}_{2}\right]^{\frac{1}{2}}} = 10^{7 \cdot 1} = \frac{\left(\text{co}_{3}\right)^{\frac{1}{2}}}{\left(\text{OH}^{-}\right)^{2}}$$
$$= 10^{22} \left(\text{co}_{3}^{-}\right)^{\frac{1}{2}}$$

It is reasonable to assume  ${\rm CO}_3^=$  to be between  ${\rm 10}^{-14}$  to  ${\rm 10}^{-16}$  M, which corresponds to a carbonic acid  $({\rm H_2CO_3})$  concentration of  ${\rm 10}^{-5}$  to  ${\rm 10}^{-3\cdot4}$  M. By substituting these numbers into the equations for R<sub>1</sub> R<sub>2</sub>, malachite  $({\rm Cu_2CO_3(OH)_2})$  appears to be the logical controlling solid in the above systems. Carbonate and hydroxide solids become unstable under acidic pH conditions. Likewise, as pH increases, soluble phase copper is expected to decrease. This probably partially accounts for the high soluble copper concentrations found in the Sayreville samples. The pH was generally higher for the fourth set of data than for the third set, and the copper showed a corresponding decrease.

306. However, from simple solubility calculations, copper should exist in concentrations orders of magnitude higher than the observed values:

$$cu^{+2} = \frac{K_{sp}^{\frac{1}{2}}}{\left[OH^{-}\right]\left[CO_{3}^{-}\right]^{\frac{1}{2}}} = \frac{10^{-16.6}}{\left(OH^{-}\right)\left(CO_{3}^{-}\right)^{\frac{1}{2}}} = 2 \times 10^{6} \text{ ppm}$$

Copper is known to form stable complexes with chloride, hydroxide, and other inorganic and organic ligands. Though not yet very well understood, the soluble organic complexes are believed to bind the majority of soluble copper. The majority of the soluble copper species are positively charged \$^{174},175\$ and are strongly adsorbed by clay minerals. Lindsay \$^{173}\$ posed the following equation to explain the high copper concentrations in some soils:

$$Cu^{+2}$$
 + soil =  $Cu$ -soil +  $2H$ 

The K value was found to be  $10^{-3.2}$ ,  $^{176}$  the copper concentration is given by:

$$Cu^{+2} = 10^{3.2} (H^+)^2$$

At pH 3, the copper concentration is calculated to be 99 ppm, much lower than the predicted value from the solubility of malachite.

307. Jenne<sup>159</sup> proposed that iron and manganese oxides provide large surface areas for sorption reactions with copper. It is also known that copper chelates strongly with humic substances.<sup>177</sup> A combination of these mechanisms probably governs the transport of copper in the oxidized environment.

308. Copper sulfide is expected to be the controlling solid in the reducing environments. The solubility product for this solid is very low. Assuming  $\begin{bmatrix} s \end{bmatrix}$  to be 20, the copper concentration is given by:

$$Cu^{+2} = \frac{K_{sp}}{s^{=}} = \frac{10^{-36.4}}{10^{-20}} = 10^{-16.4} M$$
  
= 2 x 10<sup>-7</sup> ppb

309. The following is a tabulation of the ranges of soluble copper concentrations, arranged according to oxidizing and reducing conditions:

Site	рн Range	Oxidizing, CuCO <sub>3</sub> Control	Reducing, CuS Control			
Sayreville	3 to 7	1 ppb to 11.4 ppm	1 to	145 ppb		
Pinto Island	4.8 to 8.2	1 to 345 ppb	2 to	24 ppb		
Houston	5.8 to 7.7	5 to 165 ppb	4 to	13 ppb		
Grand Haven	5.4 to 7.8	1 to 63 ppb	2 to	7 ppb		

The copper concentration is generally much lower in a reducing environment than in an oxidizing environment. The observed values are still much higher than the predicted values.

310. Complexation with other ligands can solubilize copper to a much higher total concentration than that calculated from copper sulfide solubility. Copper is known to form highly stable complexes with soluble inorganic and organic molecules. The formation constants of copper with common ligands, such as chloride, hydroxide, and sulfate, have been extensively tabulated in the literature. 178,179 However, these complexes are not expected to increase the copper concentration by more than 100 fold.

- 311. The only likely candidates for competing ligands are organic molecules. As reflected by the formation constants, copper organic complexes are much more stable than the inorganic complexes. For example, as compiled by Lu and Chen, 148 the log formation constant for Cu-histidine is 11.71 as compared with 1.58 for CuCl<sup>+2</sup>. Lerman and Childs 180 found log B for nitrilotriacetates (NTA) to be 13. The nature of soluble organics in natural waters is not very well known. It is generally believed that copper is strongly complexed with organic matter, and this is expected to play an important role in regulating the transport of copper. 173,181,182
- 312. Copper was found to be higher in the Pinto Island and Grand Haven on-site samples than in the off-site samples (Table 22). Monitoring the water quality in the groundwater table indicated that at the Pinto Island site, the wells underneath the site provided samples with the highest concentration, possibly due to leaching from the dredged material in the site. The downgradient monitoring wells had a lower average concentration (10 ppb) but were statistically higher than the background wells (Table 23). This suggests that copper might have migrated to the monitoring wells from on-site sources. Due to the various attenuation mechanisms discussed, the average concentration decreased from 41 ppb in samples obtained from beneath the site to 10 ppb for the monitoring well samples.
- 313. For the Grand Haven site, the background samples were similar in soluble copper concentration to the samples collected underneath the site (12 and 15 ppb, respectively), suggesting that either copper was not leached out or was greatly attenuated as it left the site.
- 314. In summary, leaching effects could not be established for the Sayreville site due to the high background concentrations. Both the background and the downstream samples were higher than the onsite samples. This is probably due to the formation of organic complexes. The off-site samples were shown to have higher TOC than the on-site samples.
- 315. Leaching was observed at the Pinto Island site. However, the concentration was so low that it posed no deterioration threat to the groundwater quality.

#### Nickel

- 316. Among the trace metals analyzed, other than iron and manganese, the nickel concentration was usually the highest. This is in accordance with the relatively higher solubility products of the nickel controlling solids:  $10^{-8.2}$  for NiCO<sub>3</sub> and  $10^{-18.5}$  for NiS, and  $10^{-25.7}$  for YNiS.
- 317. In the vicinity of the Sayreville site, most samples were in the hundred ppb range. The average off-site sample concentration was 237 ppb, and the average on-site sample concentration was 420 ppb. Both numbers were highest among the case study sites. Both the Grand Haven and Pinto Island sites also had higher on-site averages than the off-site averages: 128 and 27 ppb for Grand Haven, 42 and 10 ppb for Pinto Island. In most natural processes, species migrate from zones of high concentration to low concentration areas. Thus there is a potential that nickel may migrate to the groundwater from the disposal sites.
- 318. The nickel data for groundwater samples from each site are summarized in Table 23. At Pinto Island, nickel increased from 4.3 ppb in background water samples to 40 ppb in water collected beneath the site, and then decreased to 11 ppb for water in the off-site monitoring wells. The under-site samples average of 40 ppb was as high as the on-site average of 42 ppb, suggesting that groundwater directly below the site was affected. During horizontal migration of leachate (away from the site), nickel was reduced by 75 percent due to various attenuation mechanisms.
- 319. In the immediate vicinity of the Sayreville site, nickel decreased from an average of 420 ppb for the on-site samples to an average of 325 ppb for the samples collected beneath the site, an average decrease of 22 percent (Tables 22, 23). Nickel was further attenuated down gradient to an average of 237 ppb, a net average reduction of 44 percent.
- 320. The highest nickel depletion was obtained at the Grand Haven site. Due to the high background concentration, the extent of leaching could not be established. However, by comparing the onsite average in Table 22 with the under-site and monitoring well averages in Table 23, it can be seen nickel decreased from 128 ppb

for the on-site samples to 65 ppb for the under-site samples. The downgradient off-site monitoring samples averaged 22 ppb, a total reduction of 83 percent over on-site values.

- 321. The nickel migration was probably controlled by a number of mechanisms. As the dredged material was disposed of, nickel was probably transformed from nickel sulfide into nickel carbonate due to the change in the redox conditions, resulting in more nickel release. Wakeman reported an increase in nickel during dredging and open-water disposal in San Francisco Bay. An increase in the carbonate phase coupled with a decrease in the sulfide and organic phases has been observed in influent-effluent samples from dredged material disposal sites. <sup>69,144</sup>
- 322. In an oxidizing environment, the nickel concentration should be controlled by  ${\rm NiCO}_3$ , and its theoretical concentration is given by:

$$\left[\text{Ni}\right] = \frac{\kappa_{\text{sp}}}{\left[\text{Co}_{3}^{=}\right]} = \frac{10^{-8 \cdot 2}}{\left[\text{Co}_{3}^{=}\right]} = 37 \text{ ppm to } 4300 \text{ ppm}$$

Nickel also forms stable complexes with chloride, carbonate, and other inorganic and organic ligands. Chen and Rohatgi 184 suggested that the initial release of nickel from suspended particulates upon disposal into the ocean is due to the formation of soluble chloride complexes. Complexation with soluble organic ligands can further increase the theoretical soluble nickel concentration, which is already orders of magnitude higher than the observed values (Table K1 to K4).

- 323. Soluble nickel was probably adsorbed by iron and manganese oxides in oxidizing environments. Pronina et al. 185 showed that nickel can be scavenged from seawater by naturally occurring hydroxides of iron and manganese. Goldberg 186 reported that nickel is linearly related to the manganese content in Pacific Ocean ferruginous sediments. The scavenging effect of iron and manganese has also been reported by many other authors. 2, 5, 158, 159
- 324. In a reducing environment, nickel sulfide will be the controlling solid. The ion ratio suggested that sulfide would be the controlling solid when pS $^{=}$  reached 16 for (NiS) $\alpha$

$$R = \frac{\left[s^{=}\right]}{\left[co_{3}^{=}\right]} = \frac{(K_{sp}) \alpha NiS}{(K_{sp}) NiCO_{3}} = \frac{10^{-18.5}}{10^{-8.2}} = 10^{-10.5}$$

or
$$R = \frac{\left[s^{2}\right]}{\left[co_{3}^{2}\right]} = \frac{(K_{sp}) \text{ YNiS}}{(K_{sp}) \text{ NiCO}_{3}} = \frac{10^{-25.7}}{10^{-8.2}} = 10^{-17.5}$$

As discussed in the cadmium section, if one chooses  $pS^{\pm}$  to be 20, free Ni could be controlled by (NiS) $\gamma$ , this is given by:

$$\left[\text{Ni}^{++}\right] = \frac{(\kappa_{\text{sp}}) \gamma}{\left[\text{s}^{=}\right]} = \frac{10^{-25.7}}{10^{-20}} = 64 \text{ ppb}$$

This concentration is remarkably close to the observed nickel values.

325. In summary, soluble phase nickel was found to exist at relatively high levels in both the dredged material and soil interstitial waters at the Sayreville site. A few of the samples exceeded the NAS Marine Water Quality Standard of 1000 µg/l. Due to the high concentration found in the background samples, the extent of leaching cannot be established. It was deduced from the comparison of the on-site, under-site and monitoring well samples, that nickel was leached from the site. Nickel was also observed to have leached from the Pinto Island and Grand Haven sites. The concencentrations were greatly attenuated as they traveled away from the sites. However, due to the low concentration, nickel is not anticipated to pose any threat to the groundwater quality at these two sites.

#### Lead

- 326. Although lead exists everywhere in the environment, it is extremely insoluble in water. Kopp and Kroner <sup>187</sup> surveyed 876 surface water samples and found a concentration range of 2 to 140 ppb with a mean of 23 ppb lead. About 10 percent of their samples exceeded 10 ppb.
- 327. Of the samples analyzed for in this study, lead existed only in minute quantities. The concentrations ranged from a low

of below 1 ppb, found for all four sites, to a high of 80 ppb, found in two Houston samples. Most samples were below 10 ppb. For the Grand haven site, 46 of the 60 samples were below 1 ppb. Only 4 of the 306 samples (from all four sites) exceeded the  $50-\mu g/l$  drinking water limit set up by EPA.  $^{188-191}$  Compared to sources tested in Kopp and Kroner's study, it appears that dredged material disposal sites pose no danger to the groundwater quality.

328. Lead, like other trace metals, goes through different solids transformations if the redox condition is changed. Wakeman 183 reported an increase of lead during dredging operations in San Francisco Bay. However, Windom 5 found no appreciable changes in water quality during and after dredging activities near the Intracoastal Waterway in Georgia.

329. Lead carbonate has been suggested as the controlling solid in oxidizing marine environments. 192 In this study, due to the low pH and high sulfate concentration in certain samples, lead sulfate may have been the controlling solid (e.g., Sayreville). Major lead complexes include carbonate, sulfate, hydroxide and chloride. 148,192 An activity ratio diagram for lead sulfate, lead carbonate, and lead hydroxide is given in Figure 78. Sulfate was assumed to be  $10^{-2.5}$ M and the total carbon concentration to be  $10^{-3.3}$  M. It is seen that below pH 6, lead sulfate is the controlling solid. From pH 6 to 11.5, lead carbonate is the controlling solid; lead hydroxide becomes important only when pH exceeds 11.5, which was not detected in any of the samples analyzed. It was calculated for this study, that, due to the ratio of sulfate to carbonate, the free lead concentration ranges would be similar, regardless of whether lead carbonate or lead sulfate was the controlling solid. The following tabulation gives the range of soluble lead under oxidizing conditions for each site and the theoretical calculations that took into account the controlling solid and ligand complexes with sulfate, carbonate, bicarbonate, and chloride:

Site	pH Range	Actual Range Lead	Theoretical Calculation PbCO <sub>3</sub> as Control Solid,  K <sub>Sp</sub> = 10 <sup>-13.30</sup>
Sayreville	3 to 7	1 to 50 ppb	1.3 to 2 X 10 <sup>7</sup> ppb
Pinto Island	4.8 to 8.2	<1 to 7 ppb	6.3 to 1.6 X 10 <sup>6</sup> ppb
Houston	5.8 to 7.7	< 1 to 80 ppb	20 to 2 X 10 <sup>4</sup> ppb
Grand Haven	5.4 to 7.8	< 1 to 30 ppb	

330. The theoretical values are close to the observed values at high pH. Lead adsorbs strongly with clay minerals. Adsorption of metals on clay minerals was reported to occur in the following order:  $\text{Cu}^{++} > \text{pb}^{++} > \text{Ni}^{++} > \text{Co}^{++} > \text{Zn}^{++}$ . Adsorption by clay, iron, and manganese oxides probably accounted for the low lead content found in this study.

331. In summary, soluble lead was found to be in very low concentration. No leaching was observed in any sites and no leaching potential was found in any sites. It is concluded that dike disposal of dredged material will not significantly increase the soluble lead level in groundwater.

332. Zinc is a fairly abundant element. Unlike most other trace metals, small amounts of zinc are essential to life. A large quantity of zinc is used industrially, and this has a significant impact on the distribution of zinc in the environment. Lazarus et al. 193 reported an average concentration of 107 ppb zinc in rainfall collected at 32 points in the United States from September 1966 to January 1967. Hem 170 surveyed 726 filtered water samples taken from rivers and lakes in the United States and found the median concentration of zinc to be close to 20 ppb, 203 considerably less than the average value reported by Lazarus.

333. In this study, Sayreville had the highest average soluble zinc concentrations of 4.16 ppm in samples from the monitoring wells, 2.44 ppm for the on-site dredged material interstitial water samples, and 3.8 ppm for the background well water. Grand Haven, being the least industrialized of the four sites, had the lowest soluble zinc average, 0.053 ppm for the monitoring well samples, 0.058 ppm

for the on-site samples, and 0.176 ppm for the background well water. Hem 170 suggests that industrial discharge of zinc aerosols could be the major source of zinc in rainfall in the northeastern United States. Comparing the data of Lazarus et al. 193 and Hem 170 it is possible that rainfall could be a source of zinc in the above sites. One other possibility for the higher off-site and background concentrations, compared to those of the on-site Sayreville samples, is the close proximity of the entire monitored area to two heavily used highways (New Jersey Highway 35 and U.S. Highway 9). Lagerwerff and Specht 172 have shown that zinc, lead, cadmium, nickel, and lead concentrations increase in soil and vegetation adjacent to highways.

- 334. Pinto Island is the only site that showed a potential for zinc leaching from the site. The on-site average soluble zinc concentration was 0.6 ppm. The off-site monitoring well samples contained 0.072 ppm soluble zinc (Table 22).
- 335. The average zinc concentration decreased from 0.60 ppm in the on-site dredged material water samples to 0.41 ppm for the groundwater samples underneath the site and to 0.073 ppm for the off-site monitoring well samples. A total decrease of 88 percent was achieved. From a comparison of background, under-site, and monitoring well averages, it appears that the monitoring wells had been affected (Tables 22 and 23).
- 336. Like other trace metals, a number of mechanisms probably attenuate zinc as it migrates from the disposal site to the surrounding soils. These include dilution, biological effects, solids transformation, complexation and adsorption. Adsorption appeared to be the most important factor. 173,182,193
  - 337. Lindsay and Norvell 194 proposed a zinc-soil system:

$$Zn^{++}$$
 + soil =  $Zn$ -soil +  $2H^{+}$ 

in which the zinc concentration is given by:

$$\left[\operatorname{Zn}^{++}\right] = 10^6 \left[\operatorname{H}^+\right]^2$$

At pH 6, the zinc concentration is calculated to be 0.063 ppm, about five orders of magnitude less than the predicted values from solubility considerations, and is much closer to the observed values from this study.

- 338. To sum up, at the Sayreville and Grand Haven sites, soluble phase zinc concentrations were lower in the on-site dredged material than in the surrounding native soils. Only the Pinto Island site reflected a leaching potential. The average for the on-site Pinto Island sample was 0.61 ppm. The EPA drinking water standard for zinc is 5 ppm. Thus, it is concluded that zinc will not be a problem at the sites studied. Iron
- 339. Iron is one of the most abundant elements or metals in the earth's crust, having an average concentration of 56,000 ppm.  $^{179}$  In soils and sediments, iron concentrations range from a few thousand ppm to several percent.  $^{126,195}$  Similar concentration ranges were found in the soil and dredged material samples collected for this study (Tables J5 to J8).
- 340. Although iron is ubiquitous in nature, its availability is usually low. Most of the iron either exists as part of mineral crystal structures or as an oxide coating on the surfaces of particles. <sup>153,196</sup> In this study, less than 1 percent of the total iron was found to exist in the water-soluble and exchangeable fractions.
- 341. In the interstitial soil water and leachates, average iron concentrations ranged from a low of 54 ppb for the Pinto Island samples to a high of 3.5 ppm for the Sayreville samples. The statistics for the other sites are given in Table 22. In general, the concentrations correlated well with redox potential and pH. Sayreville samples had relatively low Eh and pH. These conditions are known to favor mobilization of iron. Pinto Island and Grand Haven samples had higher Eh and pH values and, consequently, lower iron concentrations.
- 342. Student's "t" tests showed that the differences in iron concentrations between the on-/off-site Sayreville samples, and between the on-/off-site Pinto Island samples were statistically insignificant (p value of > 0.9 and 0.45, respectively). An average on-site sample was higher than the average off-site sample at Grand Haven by 29 ppb, creating a leaching potential. However, except for the Sayreville samples, all were below the 0.3 ppm drinking water limit set up by EPA.

343. Iron solubility is very sensitive to Eh and pH. Gotoh and Patrick  $^{199}$  and Gambrell et al.  $^{197}$  demonstrated that, in waterlogged soil and sediments at a fixed pH, an increase in soluble iron is associated with a decrease in redox potential. At a fixed redox potential, an increase in soluble iron is associated with a decrease in pH. Lu  $^{148}$  proposed that iron is transformed during a change from reducing conditions to aerobic conditions through the following stages:

$$\text{FeS} \longrightarrow \text{FeCO}_3 \longrightarrow \text{Fe} \text{(OH)}_3 \longrightarrow \text{FeOOH} \longrightarrow \text{Fe}_2\text{O}_3$$

The wide range of soluble iron concentrations found in this study was probably due largely to the various localized conditions signified by different controlling solids. However, simple solubility calculations predict a much lower concentration than the observed values. Organic complexation is the most likely candidate to account for the gap.  $^{182}$ ,  $^{200}$ 

344. A few spots of high iron concentration were found at some monitoring stations at Sayreville. For the first sampling period, samples from background well (NJJ) contained 2500 ppm which gradually decreased to 0.17 ppm during later sampling periods. One of the off-site wells (NJG1) also had a high concentration (71 ppm) in the first sample set, which later decreased to 0.1 ppm. Another background well (NJI) decreased from 39 ppm to 0.3 ppm. An on-site sample (NJA3) and an under-site groundwater sample (NJB4) exhibited similar trends. An increase in pH in these samples was also recorded (NJJ increased from 3 to 7.2, NJG1 increased from 3 to 6.4, and NJI increased from 3 to 4.6).

345. The low pH and high soluble iron levels in the sediments at Sayreville were probably caused by the oxidation of pyrite to sulfate in the poorly buffered sediments. As air infiltrates soil, the oxidation of sulfide to sulfate proceeds as a two-stage process, resulting in an acidic soil solution:

$$2\text{FeS}_{2} + 70_{2} + 2\text{H}_{2}\text{O} \longrightarrow 2\text{Fe}^{++} + 4\text{SO}_{4}^{=} + 4\text{H}^{+}$$
 $4\text{Fe}^{++} + 0_{2} + 10\text{H}_{2}\text{O} \longrightarrow 4\text{Fe} (\text{OH})_{3} + 8\text{H}^{+}$ 

The oxidation process seems plausible since the high iron levels measured during the first sampling could be due to the inclusion of fine particulate ferric hydroxide colloids or ferrous organic complexes. The oxidation process is a very rapid reaction. However, if complexed with organic matter, the oxidation of ferrous to ferric ion could be delayed by days or even months. 200

346. In conclusion, iron transport was highly influenced by the Eh-pH of the environment, solid transformation and complexation. Soluble iron levels in the dredged material were either comparable to the surrounding environment (the Sayreville and Pinto Island sites), or were low compared with the EPA drinking water standards (the Pinto Island and Grand Haven sites). It is concluded that diked disposal of dredged material will pose no groundwater iron problem.

## Manganese

347. Manganese was the most soluble element among the trace metals studied. Out of the more than 300 samples analyzed, only a few were below 0.05 mg/l, the drinking water limit set up by EPA. 188-191 On-site averages for dredged material water samples were 1.2 ppm for the Grand Haven site, 6.4 ppm for the Sayreville site, 9.2 ppm for the Pinto Island site, and 12.3 ppm for the Houston site (Table 22). Average off-site leachate samples were also at the ppm level and ranged from a low of 1.2 ppm for the Pinto Island site to a high of 7.4 ppm for the Sayreville site (Table 22). The highest individual analysis was 68 ppm and the lowest was 0.5 ppb; both samples were found in the Pinto Island vicinity.

348. The chemical behavior of manganese is quite similar to that of iron. Like iron, manganese is almost ubiquitous in soils and sediments, the solubility is highly dependent on the redox potential and pH. As discussed before, both the redox potential and pH are highly site-specific. Although the chemistry and mineralogy of most manganese solids is not well understood, it is generally considered that, under reducing conditions, manganese will exist as sulfides or silicates. Carbonate, hydroxide, and oxide solids tend to form as the redox potential is raised.

The solubility of each solid is unique, and manganese is generally more soluble than its iron counterpart. Thus, the wide range of soluble manganese observed and the nonsignificant difference between the on-/off-site New Jersey and Grand Haven samples were expected. In general, high soluble manganese concentrations were associated with low Eh or high pH. Iron usually precipitates at a lower Eh and/or pH than manganese. It is possible that the case study sites had Eh/pH conditions that promoted the formation of manganese carbonate, which is generally favored by reducing conditions and high pH. However, iron may have still existed in the very poorly soluble oxidized form, Fe(III).

349. Assuming manganese carbonate as the controlling solid, the free manganese concentration is given in Figure 76. It ranged from a few ppm to several thousand ppm. Manganese also forms stable complexes with chloride, bicarbonate and some soluble organic molecules. This will increase the total soluble manganese concentration. Sorption with clay minerals or soil organic matter probably brings the concentration to the observed range. 168

350. The importance of iron and manganese oxides in regulating the transport of trace metals has been mentioned in other sections. In the reduced form neither iron nor manganese is an effective trace metal scavenger. As the conditions become more oxidizing, iron and manganese may eventually be oxidized to ferric oxide and manganese dioxide. This oxidation could occur when reduced sediments are dredged, mixed with overlying oxygen-rich water, and disposed in an upland disposal site where atmospheric oxygen has a better chance for infiltration. These solids are characterized by high surface areas and are effective in scavenging other heavy metals from solution. <sup>186, 197</sup> Freshly precipitated oxides and hydroxides seem to be more effective in scavenging trace metals. <sup>186</sup>

351. In conclusion, among the trace metals analyzed manganese was found to be the most soluble element. Most samples exceeded the EPA drinking water standard of 0.05 mg/l. Manganese migration was controlled to a large extent by the Eh-pH of the surrounding environment. This would make manganese a potential groundwater problem.

## Mercury

- 352. Mercury concentration in the samples was determined by the cold vapor method. Compared to the other metals analyzed, the mercury was relatively more uniform in distribution, mostly in the sub-ppb range. Average on-site concentrations ranged from 0.34 ppb for Pinto Island and Sayreville to 0.48 ppb for Houston. The highest concentration detected was 3 ppb, found at Houston. This is slightly higher than the 2 ppb drinking water standard set up by EPA. 188-191 Nevertheless, of the 200 samples collected from the four sites, only 2 exceeded this limit. This range is comparable to the findings of the U. S. Geological Survey which reported <0.1 to 6 ppb mercury for selected streams in the U. S. 202 It is thus concluded that mercury should not pose any danger if the ground-water is to be used for drinking purposes.
- 353. The solids controlling the solubility of mercury are mercury sulfide (HgS) in the reduced environment and mercury hydroxide (Hg(OH) $_2$ ) in the oxidized environment. The solubility product constants of these two solids are  $10^{-53.9}$  and  $10^{-25.4}$ , respectively. These are about 10 to 20 orders of magnitude lower than the solubility of the controlling solids of other trace metals in the corresponding redox environments. The free mercury level is given by:

$$Hg_f = \frac{10^{-53.9}}{[s^{=}]}$$
 or  $\frac{10^{-25.4}}{[OH^{-2}]}$ 

Assuming a total sulfide concentration of  $10^{-9}\text{M}$ , the following tabulation summarizes the theoretical values of free  $\text{Hg}^{++}$  at various pH levels:

H	Hg(OH) 2 Control, ppb	HgS Control, ppb
3	8.24 X 10 <sup>4</sup>	10-21.6
4	8.24 X 10 <sup>2</sup>	10-23.6
5	8.24	10-25.6
6	$8.24 \times 10^{-2}$	10-27.6
7	$8.24 \times 10^{-4}$	10-29.6
8	$8.24 \times 10^{-6}$	10-31.6

354. Mercury forms stable complexes with hydroxide, chloride, and other inorganic and organic ligands. The stability constants for hydroxide complexes have been reported to be

 $\log \beta_1 = 10.8$ ,  $\log \beta_2 = 22.4$ ,  $\log \beta_3 = 10^{21.63}$ . 78

The contribution of this ligand alone to the total mercury concentration will be:

$$\left[\mathrm{Hg}^{++}\right]$$
 Total =  $\mathrm{Hg}_{\mathrm{f}}\left\{\beta_{1}\left[\mathrm{OH}\right] + \beta_{2}\left[\mathrm{OH}^{-}\right]^{2} + \beta_{3}\left[\mathrm{OH}^{-}\right]^{3}\right\}$ 

Thus,  $[Hg^{++}]$  total will be increased more than two orders of magnitude if the pH increases by one unit.

355. Organic ligands are expected to increase the solubility of mercury even further. Fuller  $^{153}$  stated that, for the most part, mercury attenuation or movement in soil must relate to organic carbon or sulfur chemistry, either separately or together as humic substances containing sulfur. Lu  $^{115}$  and Lisk  $^{118}$  compiled information on the solubility of several trace metals. The stability constant of Hg(II) - EDTA was reported to be  $10^{21.8}$ , and  $\log_{100}$  and  $\log_{100}$  of Hg(II) - cysteine were reported to be 46.2 and 20.7, respectively.

356. It is impossible to assess the exact effect of soluble organics on metal concentrations because the nature of the organic compounds in natural waters is not yet fully understood. Nevertheless, based on the thermodynamic data on the synthetic organic molecules, it is expected that the metal concentrations will be increased by many orders of magnitude compared to the solubility product constants of the controlling solids.

357. Complexation with soil organic matter and adsorption onto inorganic sediment fractions may account for the low mercury concentrations detected in this study. Jenne 159 proposed that the adsorption of mercury, in the form of mercury-chloride complexes, onto hydrous oxides or iron and manganese may be the controlling mechanism in seawater. The scavenging effect of manganese oxides on mercury was also studied by Lockwood and Chen 203 and Krauskopf. Both reports indicate that adsorption onto hydrous oxides of manganese is an important factor regulating soluble

mercury levels. Lindberg and Harris<sup>204</sup> found that mercury was released from resuspended near shore sediments. A peak of 1.6 ppb was observed which decreased to 0.2 ppb. Mercury may be released during dredging operations.<sup>5</sup> Upon disposal on upland sites, it is expected that mercury will be immobilized by the organic matter and/or scavenged by manganese and iron oxides.

358. In summary, soluble mercury levels observed were generally in the sub-ppb range. The on-site dredged material mercury levels were similar to the off-site soil mercury levels. Hence, there was no leaching potential in the study sites. Adsorption was probably the greatest attenuation mechanism in reducing the mercury levels. It is concluded that diked disposal of dredged material will not make mercury a groundwater problem.

## PART IV: CONCLUSIONS AND RECOMMENDATIONS

- 359. Analytical results of the field leachate study indicate that upland dredged material disposal should be a carefully controlled practice. Under certain conditions, leachates from upland disposal areas may degrade underlying site groundwaters. It has been demonstrated that potential adverse water quality impacts will most likely be due to the increases of chloride, potassium, sodium, calcium, total organic carbon , alkalinity, iron, and manganese. The extent of the potential impact was found to be functions of the physiochemical properties of the disposed dredged material, sitespecific groundwater hydrogeological patterns, and environmental conditions of the area surrounding the site. The field monitoring of the case study sites revealed low concentration levels of cadmium, copper, mercury, lead, zinc, phosphate, and nickel may reach groundwaters; however, concentrations of these constituents were detected at levels that should not pose water quality problems.
- and soil were similar from each of the case study sites. This was not the case, however, with soluble and exchangeable fractions, indicating bulk analysis is probably not a suitable tool for evaluating upland dredged material disposal. In general, the examination of vertical and lateral differentiations of dredged material within each of the case study sites failed to reveal any systematic changes. For any particular parameter, both increases and decreases in values occurred at different locations as well as at different depths within each site. Results of the particle size analysis of the dredged material suggested that the material in upland disposal areas is slightly more sandy than original bottom sediments. The reason for the difference might be due to the fact that finer particles tend to be carried with effluents to receiving waters due to insufficient residence time and/or turbulence.
- 361. In analysis of the interstitial water of the dredged material at each of the case study sites, no soluble chlorinated hydrocarbons/pesticides were detected. It is likely that these contaminants will probably not migrate from upland dredged material

disposal areas. However, this was not the case for many other parameters. Concentrations in the soluble phase of the water samples obtained from groundwaters below and downgradient from the case study sites showed that chloride, sodium, and potassium could pose problems to water quality. The dilution effect was found to be the major mechanism which controlled concentration of these constituents in leachates. Ion exchange was also found to regulate sodium and potassium levels. High levels of chloride in the leachates from sites containing saline dredged material may present water quality problems should leachates and/or impacted groundwaters be discharged to freshwater environments.

- 362. Analytical results from the field study indicate that both saline and freshwater upland dredged material disposal sites can increase the concentrations of calcium and magnesium in underlying site groundwaters. It was found that the concentration of calcium was controlled by ion exchange and dissolution of calcite. The possible controlling mechanisms for magnesium migration were dissolution of magnesium solids and ion exchange. The increase of hardness (mostly for calcium and magnesium), will reduce the utility of water for many beneficial uses.
- 363. Alkalinity levels in leachates were found to be increased, possibly due to dissolution of calcite, as well as biological action. TOC exhibited trends in mobility that were similar to alkalinity. Levels of TOC in leachates were affected by biological action and interactions with clay minerals. High levels of TOC in leachates pose many unknown effects. TOC in leachates may serve to mobilize trace metals from underlying site soils.
- 364. It can be concluded from data of trace metals that only manganese and possibly iron should pose water quality problems in upland dredged material disposal. Levels of the two constituents in on-site leachate samples and downgradient groundwater samples often exceeded EPA drinking water standards by a wide margin. Both iron and manganese levels were related to Eh and pH values of the various water samples. Eh and pH of the surrounding site environment, solid transformation, and complexation with organic matter all affect the soluble concentrations of iron and manganese.

- 365. Analytical results indicated that phosphate, cadmium, copper, lead, nickel, mercury, and zinc should not pose potential problems for groundwater as a result of upland dredged material disposal. The controlling mechanisms for phosphate and many of the trace metals was adsorption. Complexation and precipitation/dissolution also played a role in regulating these trace metal concentrations in leachates. From these results, it is felt that native soils in areas to be developed as dredged material disposal sites should have high sorptive capacities. This will help minimize the trace metal mobilization problems.
- 366. From the preceding discussion, it can be seen that leachates from upland dredged material disposal could have caused degradation of local groundwaters at the case study sites evaluated in this study. Upland dredged material should be a carefully controlled practice. In light of this, it is recommended that topics to be persued are as follows:
  - chronological extension of field leachate study at case study sites.
  - determination of the physical area of influence of the leachate plume from actual case study sites.
  - monitoring of groundwaters surrounding existing confined disposal sites.
  - instigation of leaching studies over extensive time periods.

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TABLE 1. PERCEIVED PHYSICAL CHARACTERISTICS AT GRAND HAVEN, MICHIGAN

		Dred	Dredged Materials	ials	Size	Size Characteristics	istics
Topographical Setting	Hydrological Setting	Material Matrix	Origin	Aquatic Environment	Setting	Size	Depth
Located on the banks of Grand Haven Harbor in Michigan; Marbor empties into Eake Michigan 2 2 mi from the	Low gradient groundwaters flowing through the site and into the harbor and low marsh area to	Silts and Sands	Harbor at Grand Haven	Freshwater	Wind- blown sands: uniform clay at 6 m (20 ft)	2.42 ha ] (6 ac) t (7	1.5 m (5 ft) to 3 m (10 ft) prior to 3/77 2.1 m (7 ft) to 3.9 m (13 ft)

TABLE 2. FIELD INVESTIGATIONS AT GRAND HAVEN, MICHIGAN

Date of Field Investigation		S	Specific Hydrological Studies Performed	Physical Conditions at the Site
November 4, 1976	92	• ••	Initial reconnaissance; surface hydrological features studied (drainage, ditches, phreatophyte study, topographic features, etc.).  Resistivity survey conducted. Installation of nine 1-1/4-in metal well points, one on-site/eight offsite; wells developed, labeled, painted, and surveyed for absolute elevation; series of water level readings obtained from each well point and plotted with time vs. water level to define effect of Grand River upon water well measurements. Contours plotted and prospective pumping well locations studied. Boring logs were made and representative samples obtained for laboratory testing.	Little on-site vegeta- tation; snowing during visit.
December 1, 19	197.6	• • •	Sampling devices placed; four stations on-site/six off-site. Wells developed, labeled, painted, and surveyed for absolute elevation. Series of water level measurements taken in sampling devices and well points.  One 6 m (50 ft) pumping well (MP) and one 6 m (50 ft) observation well (MO) installed; boring logs recorded.  Water samples collected from sampling devices.	Snow and extremely cold temperature.

(continued)

TABLE 2. (continued)

Date of Field Investigation	Specific Hydrological Studies Performed	Physical Conditions at the Site
April 8, 1977	<ul> <li>Pumping test wells and two monitoring well points were installed within the confines of the dredged material.</li> </ul>	Dredging onto site was occuring. On-site area completely ponded with
	Pumping tests attempted within the dredged material, but failed due to clogging of the well by dredged sediments.	water and several feet of sediments.
	<ul> <li>Water level eleveations obtained from well points and sampling devices.</li> <li>Water samples obtained from sampling devices.</li> <li>Extensions to on-site monitoring devices performed</li> </ul>	
May 30, 1977	• Water samples obtained along with level elevations recorded from the well points and monitoring wells.	Site dewatered; dikes bulldozed leaving entire site level.
August 5, 1977	<ul> <li>Water samples obtained along with water level elevations recorded from the well points and monitoring wells.</li> </ul>	Raining during visit; luxuriant on-site vege- tation; up to 2.4 m (8 ft) the southern area; entire site cov- ered with vegetation.

TABLE 3. CLIMATOLOGICAL DATA, MUSKEGON AIRPORT

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Beans and extremes are from the existing location. Annual estremes have been exceeded at other locations as follows. Lowest temperature -30 is February 1899; minimum monthly precipitation 0.04 is Moreaber 1904; maximum precipitation in 24 hours 5.08 is June 1921.

TABLE 4. PERCEIVED PHYSICAL CHARACTERISTICS AT SAYREVILLE, NEW JERSEY

Topographical Setting	Hydrological Setting	Material Matrix	Origin	Aquatic Origin Environment	Geologic Setting	Size	Depth
East coast of	Groundwaters	Silts	Raritan	Raritan Salt water	Quarter-	17 ha	
New Jersey; located at	manifested in standing	clays	Kiver		river	(44 ac)	to 7.9
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The Raritan	hydraulic						
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into Raritan	and innun-						
Bay and then	dates low						
into the	lying marsh						
Atlantic	areas.						
Ocean; 5 mi	Groundwater						
to the east.	may be						
	monuded under						
	the site.						

TABLE 5. FIELD INVESTIGATIONS OF SAYREVILLE, NEW JERSEY

Date of Field Investigations	ions		Specific Hydrological Studies Performed	Physical Conditions at the Site
November 12,	12, 1976	9	Initial reconnaissance; surface hydrological features mapped (i.e., streams, drainage ditches, phreatophyte survey, topographic features affecting site). Ten 1-1/4-in well points (two on-site/eight off-site) installed; wells developed, labeled, painted, and surveyed for absolute elevation; series of water level readings obtained from each well point and plotted with time vs. piezometric level to define effect of tide upon water well measurements. Contours plotted and prospective pumping well locations studied. Boring logs made and representative samples obtained for laboratory testing.	Wet from recent rain; little on-site vege- tation.
November 28,	28, 1976	9	On-site sampling devices placed; four stations on-site/six off-site. Wells developed, labeled, printed, and surveyed for absolute elevation. Series of water level measurements taken in sampling devices and well points. One 15 m (50 ft) pumping well and one 15 m (50 ft) observation well installed; boring logs recorded; preliminary pumping test performed. Water samples collected from sampling devices.	Snowing and raining during sampling

(continued)

TABLE 5. (continued)

Date of Field Investigations	Specific Hydrological Studies Performed	Physical Conditions at the Site
November 28, 1976 (con'd)	<ul> <li>Pumping test wells and two monitoring well points installed within the confines of the dredged material.</li> </ul>	
	<ul> <li>Pumping test attempted within the dredged material, but failed due to clogging of well by dredged sediments.</li> </ul>	
April 6, 1977	<ul> <li>Water level elevations obtained from well points and sampling devices.</li> <li>Water samples obtained from sampling devices.</li> <li>Extensions to on-site monitoring devices performed.</li> </ul>	Dredging site being prepared for dredging; dike height increased.
June 2, 1977	<ul> <li>Water level eleveations obtained from well points and sampling devices.</li> <li>Water samples obtained from sampling devices.</li> </ul>	Dredging occurring; several feet of water covering the entire site along with several feet of sediment.
August 5, 1977	<ul> <li>Water level elevations obtained from well points and sampling devices.</li> <li>Water samples obtained from sampling devices.</li> </ul>	Light rain; no on-site vegetation.

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House and extremes in the above table are from existing or comparable location(s). Annual extremes have been exceeded at other locations as follows:

Lowest temperature -14 in February 1934; maximum monthly precipitation 22.48 in August 1843; minimum monthly precipitation 0.07 in June 1949.

TABLE 7. PERCEIVED PHYSICAL CHARACTERISTICS AT HOUSTON, TEXAS

		Dredged Materials	aterials		Size Characteristics	cteristi	CS
Togographical Setting	Hydrological Setting	Material Matrix	Origin	Aquatic Environment	Geologic Setting	Size	Depth
Upland area	Essentially an artifical system within the site: disposal pond underlain by native clays: perched water above clays moves through dredged material and collects in surface ponds in the north section.	Clays and sands	Houston Ship Channel	Saline and Freshwater	Geosyn- 1. clinal (2. area; native sedi- ments Quarter- nary sands and clay; Houston clay predominates at surface in vicinity	111 ha 6 m (275 ac) (20 ft) m (35 ft) ft) s s s s s ty	6 m (20 ft) to 10 m (35 ft)

TABLE 8. FIELD INVESTIGATIONS AT HOUSTON, TEXAS

Date of Field Investigation	Specific Hydrological Studies Performed	Physical Conditions at the Site
November 6, 1976	<ul> <li>Initial reconnaissance; surface hydrological features mapped (i.e., streams, drainage ditches, phreatophyte survey, topographic features affecting site).</li> <li>Installation of 10 3.1 cm (1-1/4-in) well points, 2 on-site/8 off-site; well developed, labeled, painted, and surveyed for absolute elevation; series of water level readings obtained from each well point and plotted as time vs. water level to define fluctuations in wells with other site variables (e.g., ponding). Contours plotted and prospective pumping well locations studied. Boring logs were made and representative samples obtained for laboratory testing.</li> </ul>	On-site vegetation scarce; essentially bare; approximately 1/2 site flooded
December 7, 1976	<ul> <li>On-site sampling devices placed; four on-site/six off-site. Well developed, labeled, painted, and surveyed for absolute elevation. Series of water level measurements taken in sampling devices and well points.</li> <li>Two 10 m (35 ft) off-site pumping wells and one 10 m (35 ft) observation well installed; boring logs recorded; preliminary pumping test performed.</li> <li>Water samples collected from sampling devices.</li> </ul>	Little on-site vegeta- tion; ponded water re- duced from previous visit.

(continued)

TABLE 8. (continued)

Date of Field		
Investigation	specific Hydrological Studies Performed	at the Site
December 7, 1976 (con'd)	<ul> <li>Pumping test well and one monitoring well were installed within the confines of the dredged material.</li> <li>Two pumping test wells and one monitoring well were installed off-site.</li> </ul>	
	<ul> <li>Pumping test attempted within the dredged material, but failed due to clogging of the well by dredged sediments.</li> </ul>	
March 25, 1977	<ul> <li>Water level elevations obtained from well points and monitoring devices.</li> <li>Water samples obtained from sampling devices.</li> </ul>	Conditions unchanged.
June 12, 1977	<ul> <li>Water level elevations obtained from well points and monitoring wells.</li> <li>Water samples obtained from sampling devices.</li> <li>Off-site pumping test conducted.</li> </ul>	On-site vegetation dense; in some areas as much as 7 or 8 ft. Onsite wells difficult to locate.
July 30, 1977	<ul> <li>Water level elevations obtained in well points and monitoring wells.</li> <li>Water samples collected.</li> </ul>	On-site vegetation dense; extremely humid.

CLIMATOLOGICAL DATA FOR GALVESTON POST OFFICE BUILDING 6 TABLE

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\$ Through 1967. . 1 \$ Through 1964.

TABLE 10. PERCEIVED PHYSICAL CHARACTERISTICS AT PINTO ISLAND, ALABAMA

		Dred	Dredged Materials	als	Site Characteristics	aracteri	stics
Topographical Setting	Topographical Hydrological Setting	Material Matrix	Origin	Aquatic Environment	Geologic Setting Size	Size	Depth
Man-made island	Essentially a radial flow from center of island	Sands and Silts	Mobile Bay	Salt	Sands or 50 ha 4.5 m Silts (125 ac) to 60 m (20 ft)	50 ha (125 ac)	4.5 m to 60 m (20 ft)

TABLE 11. FIELD INVESTIGATIONS AT PINTO ISLAND, ALABAMA

January 17, 1977	Specific Hydrological Studies Performed	at the Site
	• Reconnaissance of site's hydrology (drainage ditches, phreatophytes, topography). On-site sampling devices placed; four on-site, six off-site. Wells developed, labeled, painted, and surveyed for absolute elevation. Series of piezometric measurements obtained from sampling devices. Water samples collected from sampling devices.	Vegetation scarce. Snowed during the installation of the monitoring devices.
March 26, 1977	• Piezometric elevations obtained from sampling devices. Water samples obtained.	Dredging conducted during visit; on-site wells above ponded waters; discharge pipe located northwest corner of the site; moved to area $\approx 200$ ft west of DI-D.
June 7, 1977	<ul> <li>Piezometric elevations obtained from sampling devices. Water samples obtained.</li> </ul>	Site dewatered signi- ficantly from previous visit.
August 1, 1977	• Piezometric elevations obtained from sampling devices. Water samples obtained. Off-site pumping test conducted.	Light rains; area very dry.

CLIMATOLOGICAL DATA FOR BATES FIELD TABLE 12.

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TABLE 13.
SHIPPING/SAMPLING CATEGORIES AND
POTENTIAL METHODOLOGIES EVALUATED

Gen	eral Categories	Potential Methodologies (Ref.)
Α.	Dredged Material Sampling	
	1. Coring	Post hole digger (22,23,30) Hand auger (22,23,25,30) Power auger (23,24,25,26,50) Truck mounted drilling rig (28,34,35,59) Hydraulic porta-sampler(22,61) Water jetting (29, 36, 50, 57, 56) Excavation (50)
В.	<ol> <li>Collection</li> <li>Background Soil Sampling</li> </ol>	Denison sampler (22,49,50,62) Osterberg piston sampler (22, 49, 50,58) Hand piston sampler (22,49,50,62) Posthole auger (49,65) Split tube sampler (49,61,62) Sand pump sampler (34,48,61) Split spoon with trap valve(22,36,61,62)
ь.	Background Soil Sampling	
	1. Coring	Posthole digger (22,50) Hand auger (22,25,50) Power auger (23,24,26,50) Truck mounted drilling rig (28, 34, 35,49) Hydraulic porta-sampler (22,61) Excavation (50)
	2. Collection	Denison sampler (22,49,60,62) Osterberg piston sampler (49,60,62) Hand piston sampler (22,47,60,62) Posthole auger (49,65) Split tube sampler (22,49,61,62) Sand pump sampler (24,48,61) Split spoon with trap valve (22, 36,61,62)
c.	Interstitial and Groundwat Sampling	
	1. Interstitial	Pressure/vacuum lysimeter (27,34,38 39,43,46,63)
	(Co	ontinued)

TABLE 13. (Continued)

Ger	neral Categories	Potential Methodologies (Ref.)
c.	Interstitial and Groundwate Sampling (cont'd)  1. Interstitial Water	Hand vacuum pump (40,51,64) Gas driven vacuum pump (43,44,51,6
		Electric vacuum pump (43, 44, 51,6467)
	2. Groundwater	PVC well point (27,34,37,42,47,55 56) PVC well with screen (27,37,45,55 Metal well point(37, 45,55) Pitcher pump (32,52,55) Johnson portable sampler(30,31,32
		33,53) Bailing method (48,54,55,64) Pressure/vacuum system (64,67) Gas driven vacuum/pressure pump (43,44,51) Electric vacuum pump (43,44,51, 64,67)
D.	Sample Containers for Soils, Dredged Materials and Water	
	1. Selection	
	Soils	Glass containers/bottles Plastic bottles Grab bags Soil tubes (PVC metal)
	Dredged Material	Grab bags Soil tubes Plastic bottles Glass containers
	Water samples	Glass bottles Plastic bottles
	2. Preparation	Acid wash Rinsing
E.	Shipping Procedures	
	1. Soils	Air freight routing Shipping boxes (styrofoam, wooden ice chests, etc.)

TABLE 13. (Concluded)

General Categories

Potential Methodologies (Ref.)

E. Shipping Procedures (con'd)

2. Water

Air freight routings
Ice chests
Styrofoam boxes
Wooden boxes

TABLE 14. SELECTED SHIPPING AND SAMPLING METHODOLOGIES

Gen	eral	Categories	Potential Methodologies
Α.	Dre	dged Material Sampling	
	1.	Coring	Hand Augers
	2.	Collection	Present techniques inadequate
в.	Soi	1 Sampling	
	1.	Coring	Hand augers
	2.	Collection	Present techniques inadequate
c.		erstitial and Groundwater	
	1.	Interstitial	Pressure/vacuum lysimeter
	2.	Groundwater	PVC well point
D.		ple Containers for Soil/ dged Material & Water	
	1.	Selection	
		Soils Dredged Material Water Samples	Present techniques inadequate Present techniques inadequate Glass/plastic
	2.	Preparation	
		Soils Dredged Material Water Samples Collection devices	Acid wash followed with distilled water rinse
	3.	Shipping	
		Soil Water	Air freight plastic sample tubes in wooden boxes, air freight sample bottles in ice chest and cardboard, styro- foam-lined boxes

TABLE 15. SAMPLE CONTAINERS AND PREPARATION

Material	Preparation Procedures	Test Performed
Polvethvlene bottle	Soaked in 5 per- cent HNO <sub>3</sub> for 24 hr rinsed with ultra-pure water	Trace metals
Polyethylene bottle	Rinsed several times with dis- tilled water; 5ml of zinc acetate added for fixation	Sulfides
Glass bottle	Rinsed twice in distilled water	Miscellaneous constituents
al		
ABS	Acid rinse with 7 percent HCl. Rinsed twice with distilled water	
ABS	Sames as for dredged materials	
	Polyethylene bottle  Polyethylene bottle  Glass bottle  ABS	Polvethylene bottle  Polyethylene bottle  Polyethylene bottle  Polyethylene bottle  Polyethylene bottle  Polyethylene bottle  Rinsed several times with distilled water; 5ml of zinc acetate added for fixation  Glass bottle  Rinsed twice in distilled water  ABS  Acid rinse with 7 percent HCl. Rinsed twice with distilled water  ABS  Acid rinse with 7 percent HCl. Rinsed twice with distilled water

TABLE 16 . PREPARATION OF FIELD EQUIPMENT

Item	Function	Preparation Procedures
Pressure/vacuum lysimeter	Collects interstitial water	Saoked in 5 percent HCl solution for 14 hr, rinsed twice with distilled water; once with ultra-pure
Pressure/vacuum lysimeter tubing	Sample water drawn through tubes from lysimeter into collection bottle	Sames as for lysimeter preparation
PVC well points	Groundwater col- lection	Rinsed twice with dis- tilled water
Glass water collection	Water collected from subsruface devices into this bottle	Soaked in 5 percent HCl solution; rinsed twice with distilled water and once with ultrapure water
Polyethylene tubing	Water drawn through tubing into glass collection bottle	Same as for lysimeter preparation

TABLE 17. PHYSICAL CHARACTERISTICS OF FOUR CASE STUDY SITES

Site	Surface Flow Patterns	Groundwater Flow Patterns	Native Soils & Geologic Age	Topographical Setting	Geograph- ical Location	Dredged Material Origin	Annual Average Precipitation	<b>Dredged</b> Area	Dredged Material Area Depth
Sayre- ville, N. J.	From NW to ponded area in E. sector; drainage to age to Raritan River from NE sector. From effluent river to Raritan River.	Radial flow from site; perched condition; complex model.	Unstratified Quarternary sands & silts (Ref.18)	Upland; ad- jacent to maritan River.	East	Salt-wedge estuary and river- rine	(Ref. 8)	44 ac	30. 30.
Grand Haven, Mich.	From N to S; drainage to Grand River from SW corner; no ponding- Flows across site and into bay through	Gentle, gradient flowing thru site t toward river.	Aeolian sands; Peninsula uniform clay at 20'; frac- tured Paleo- zoic sand- stone and shale bedrock (Ref.11)	Peninsula	North- east	Freshwater	32" (Ref. 8)	ن به پ	5. 10.

TABLE 17. (Concluded)

Dredged Material rea Depth	35.	15' to 20'
Dredged	275 ac	65 a n
Annual Average Precipitation	60" (Ref. 8)	64" (Ref. 8)
Dredged Material Origin	Mixed brackish f fresh- conditions (ship chan- nel)	Salt-wedge estuary & riverrine
Geograph- ical Location	South	South- east
Topographical Setting	Upland; inland site	Island in Mobile Bay
Native Soils & Geologic Age	Clays of low permeability, isolating site from regional aquifer. (Ref.19)	Interstrati- fied recent sands and silts; mostly sand off-site (Ref.21)
Groundwater Flow Patterns	Local isolated system: area underlain by native clays; perched water above clays moves thru dredged material, toward ponded area.	Essentially a radial flow away from the site.
Surface Flow Patterns	From S & SE upland to pond in N sector; drainage to drainage to distribute thru weirs weirs flows across site and ponds.	Pinto From N and Island, NW to Ala. Phallow ponding along E 6 S sections; drainage to Mobile Bay from S end of site. Flows across site and ponds.
Site	Hous- ton, Tex.	Pinto Island Ala.

TABLE 18. HYDRAULIC CONDUCTIVITY VALUES

Parameter	Site and Location		Number of Samples	Raj	Range	Mean	Standard Deviation
	Grand Haven	BG OS	2 12 8	9.1 x 10 <sup>-4</sup> - 1.4 x 10 <sup>-3</sup> 1.2 x 10 <sup>-6</sup> - 3.0 x 10 <sup>-3</sup> 6.6 x 10 <sup>-6</sup> - 5.2 x 10 <sup>-3</sup>		1.2 x 10 <sup>-3</sup> 2.7 x 10 <sup>-4</sup> 1.8 x 10 <sup>-3</sup>	8.6 x 10-4 2.2 x 10-4
Hydraulic	Sayreville	BG OS	12	7.3 x 10 <sup>-5</sup> - 4.5 x 10 <sup>-3</sup> 2.5 x 10 <sup>-7</sup> - 2.1 x 10 <sup>-5</sup> 2.5 x 10 <sup>-7</sup> - 1.1 x 10 <sup>-5</sup>	4.5 x 10 <sup>-3</sup> 2.1 x 10 <sup>-5</sup>	2.3 x 10 <sup>-3</sup> 5.1 x 10 <sup>-6</sup>	5.7 x 10-6
conductivity cm/sec.	y Houston	SO	26	1.5 x 10 <sup>-8</sup> - 2.1 x 10 <sup>-4</sup>	2.1 x 10 <sup>-4</sup>	1.8 x 10 <sup>-5</sup>	4.5 X 10 4.4 X 10 <sup>-5</sup>
	Pinto Island BG OS MW	BG OS MW	1 12 9	8.6 x 10 <sup>-7</sup> - 1.4 x 10 <sup>-4</sup> 5.4 x 10 <sup>-7</sup> - 9 x 10 <sup>-5</sup>	1.4 x 10-4 x x 10-5	3.6 x 10 <sup>-5</sup> 7.1 x 10 <sup>-5</sup> 3.7 x 10 <sup>-5</sup>	1.0 × 10 <sup>-4</sup> 3.5 × 10 <sup>-5</sup>

TABLE 19. STATISTICAL CHARACTER OF DREDGED MATERIAL/SOIL SAMPLES

Parameter	Site and Location		Number of Samples	Range	Mean	Standard Deviation
	Grand Haven	BG	1	_	6.8	-
		os	12	4.7-8.0	6.7	0.9
		MW	7	4.6-7.4	6.5	1.0
	Sayreville	BG	21	-	7.3	-
		os	10	5.776	6.8	0.8
рН		MW	7	6.0-7.5	6.6	0.6
pii.	Houston	BG	26	6.3-7.2	6.7	0.4
	Pinto Island	d BG	1	-	7.6	-
		os	12	5.1-7.2	6.5	0.8
		MW	9	6.4-7.6	7.0	0.4
					105	
	Grand Haven		21	242 . 222	185	•
		os	12	-249-+290	_	-
		MW	8	177-+253		
	Sayreville	BG	1	-	350	-
		os	11	-360-+284	-	
Eh, mV		MW	7	-260-+346	•	
	Houston	os	26	-254-+102	-	- *
	Pinto Island	BG	1		+214	-
		os	12	-232-+353	-	-
		MW	9	- 82-+368	-	-
	Grand Haven		2	1-2	1.5	-
		os	12	8-84	42	27
		MW	8	1-58	19	19
	Sayreville	BG	2	6-61	33	-
		os	12	7-77	55	25
Cation exchange		MW	8	9-66	47	18
capacity	Houston	os	26	1.9-21	14	11
meq/100 g	Pinto Island	BG	1	-	1.8	-
		os	12	0.54-51	11	18
		MW	9	0.45-29	8.9	11
		(0	Continued)			

TABLE 19. (Continued)

Parameter	Site and Location		Number of Samples	Range	Mean	Standard Deviation
	Grand Haven	BG OS	2 12	456-481 279-3891	469 1747	-
		MW	8	122-1759	766	870
	Sayreville	BG	2	224-2961	1592	-
Oil and grease,		os MW	12 8	247-5460 400-5252	2327 3070	1650 1679
mg/kg	Houston	os	26	169-4505	1131	1116
	Pinto Island		1	-	555	-
		os MW	12 9	351-4370 382-938	1358 512	2109 169
	Grand Haven	BG	2	405-721	536	
		os	12	272-5078	1718	1478
		MW	8	135-2028	923	642
	Grand Haven		2	405-721	563	-
		os MW	12 8	272-5078 135-2028	1718 923	1478 642
	Sayreville	BG	2	1580-1642	1611	-
Total		OS MW	12 8	395-2336 202-3493	1490 1662	787 1245
phosphorus, mg/kg						
mg/ kg	Houston	os	26	379-3142	1281	864
	Pinto Island		1	-	555	-
		os MW	12 9	351-4370 382-938	1358 512	2109 169
	Grand Haven	BG	2	3-7	5	-
		os MW	12 8	8-86 2-72	43 24	33 31
	Sayreville	BG	2	5-58	32	
Moisture		OS	12 8	4-83 45-87	65 74	22 14
equivalent (percent)	Houston	os	26	6-38	20	9
	Pinto Island	BG	1	_	3	
		OS MW	12	3-38 3-47	14 16	13 16

TABLE 19 . (Continued)

Parameter	Site and Location		Number of Samples	Range	Mean	Standard Deviation
	Grand Haven	A B C	2 12 8	0.23-0.61 0.60-11.3 0.01-8.5	0.42 3.8 2.5	3.3 3.3
Total organic	Sayreville	A B C	2 12 8	0.48-1.4 0.02-2.8	0.94	0.95
carbon (percent)	Houston	В	26	0.01-1.1	0.27	0.27
(percent)	Pinto Island	A B C	1 12 9	0.22-2.71 0.08085	0.63 0.97 0.53	0.71 0.31
	Grand Haven	A B C	2 12 8	72-160 918-5481 504-5808	116 2586 2890	- 1689 2385
Total Kjeldahl	Sayreville	A B C	12 8	411-7686 1883-4911 1188-3800	4345 3170 2630	1004 1005
nitrogen,	Houston	В	26	51-1033	363	262
mg/kg	Pinto Island	A B C	1 12 9	- 38-963 80-522	134 269 222	284 156
	Grand Haven	A B C	12 8	-19 7-200 5-33	9.8 53 18	52 11
Acid- soluble	Sayreville	A B C	12 8	15-67 33-445 -2357	41 169 551	128 815
sulfide, mg/kg	Houston	В	26	12-670	100	151
	Pinto Island	A B C	1 12 9	4-144 2-147	9 35 22	41 47

TABLE 19. (Concluded)

Parameter	Site and Location		Number of Samples	Range	Mean	Standard Deviation
	Grand Haven	BG	2	1.6-1.7	1.7	-
		OS	12	1.5-2.2	1.7	0.21
		MW	8	1.3-2.0	1.7	0.23
	Sayreville	BG	2	_		_
Bulk		os	12	1.2-1.9	1.6	0.20
density,		MW	8	1.3-1.8	1.5	0.18
gm/c.c.	Houston	os	26	1.6-2.2	1.9	0.14
	Pinto Island	BG	1	<u> </u>	-	_
		os	12	1.3-2.1	1.7	0.25
		MW	9	1.4-2.1	1.8	0.21

TABLE 20. Chlorinated Hydrocarbons in Dredged/Material/Soil Samples

Parameter	Site & Location	ocation	Number of Samples	Range	Mean	s. b.
	Pinto Island	96	-	:	0.8	:
		90	12	10.6 - 512.5	78.0	139.8
		75	6	2.69 - 0	9.01	22.4
	Sayerville	98	2	6.34 - 30.0	18.17	:
		90	12	15.89 - 242.0	96.1	89.9
Total DDT,		<b>M</b> 5	<b>&amp;</b>	42.2 - 627.0	196.9	200.3
qd	Grand Haven	98	2	5.8 - 16.3	10.8	1
		SO	12	5.7 - 143	44.2	38
		35	<b>&amp;</b>	4.0 - 60.3	29.6	23
	Houston	90	22	0 - 851.2	67.2	179.5
	Pinto Island	98	-		0	1
		SO	12	0.011- 2.7	0.36	0.78
		3	6	0 - 0.024	0.01	0.01
	Sayerville	98	2		0.011	:
otal DrR		08	12	0.022- 2.21	0.58	0.54
ddd		75	<b>&amp;</b>	0 - 1.01	0.316	0.371
	Grand Haven	8G 6W	2 2 8	0.13 - 0.13	0.13	111
	Houston	SO	22	0 - 288	0.22	0.61

TABLE 20. (Concluded)

Parameter	Site & Location	cation	Number of Samples	Range	Mean	S. D.
	Pinto Island	96	-2	0 - 2.2	0.4	1 6
Dieldrin,		35	i e	9.0 - 0	0.07	
qdd	Sayerville	96	2	0.2 - 0.7	0.45	1
		08	12	1.2 - 5.0	2.26	1.19
		A5	80	0.3 - 8.1	17.7	2.35
	Grand Haven	98	2	0.2 - 0.2	0.2	1
		08	12	0.5 -	1.18	0.91
		A5	80	0.4 - 3.7	1.53	
	Houston	90	22	0 - 4.2	0.83	1.35

TABLE 21.

CONCENTRATION OF TOTAL DISSOLVED SOLIDS

SITE	LOCATION	TDS, mg/l
Pinto Island	Background On-Site Off-Site	274 6182 1164
Sayreville	Background On-Site Off-Site	4388 17027 5417
Grand Haven	Background On-Site Off-Site	848 1866 1675
Houston	On-site	9973

TABLE 22. STATISTICAL CHARACTER OF LEACHATE/INTERSTITIAL WATER

Parameter	Site and Location		Number of Samples	Range	Mean	Standard Deviation	Probability p Value On-site vs. Off-site
	Grand Haven	BG OS	4 16 24	7-560 80-610 140-530	188 356 321	252 134 99	0.35
Calcium,	Sayreville	BG OS	8 32 29	2-140 50-623 9-754	27 386 141	47 140 161	<0.01
mg/l	Houston	SO	82	250-1020	428	185	1
	Pinto Island	BG OS MW	3 39 24	31-81 25-440 2-166	56 140 74	25 108 50	<0.01
	Grand Haven	BG OS MW	6 17 24	8-75 47-112 13-90	31 71 43	26 17 18	<0.01
Magnesium, mg/l	Sayreville	BG OS MW	32 28 28	4-362 195-1040 7-734	98 728 237	117 184 199	<0.01
	Houston	SO	81	100-845	394	128	-
	Pinto Island	BG OS	3 40 26	1-40 10-950 2-140	14 174 39	22 192 46	<0.01

(Continued)

TABLE 22 (Continued)

Parameter	Site and Location	2	Number of Samples	Range	Mean	Standard Deviation	Probability p Value On-site vs. Off-site
	Grand Haven	BG OS MW	6 19 24	3-39 5-110 1-30	13 29 11	14 28 7	< 0.01
Potassium, mg/l	Sayreville	BG OS MW	33 29	1-923 99-959 12-680	127 256 168	322 152 188	< 0.04
	Houston	SO	82	13-677	168	180	1
	Pinto Island	BG OS MW	3 26	1-3 6-330 3-180	2 81 32	1 70 45	< 0.01
Sodium,	Grand Haven	BG OS MW	6 17 24	9-20 32-790 6-500	13 110 60	4 177 96	0.25
mg/1	Sayreville	BG OS MW	8 33 29	25-1700 2000-5000 75-3490	520 4310 1664	597 1262 1433	< 0.01
	Houston	SO	82	650-4850	2690	850	-
	Pinto Island	BG OS MW	3 40 26	5-30 19-5800 2-1500	14 1485 221	14 1490 345	< 0.01

TABLE 22 (Continued)

Crand Haven OS IT OS IT OF CALLOR OS IT OS IT OF CALLOR OS IT OS IT OS IT OF CALLOR OS IT OS IT OF CALLOR OS IT OS	Parameter	Site and Location	Nu S	Number of Samples	Range	Mean	Standard Deviation	Probability p Value On-site vs. Off-site
Fide, Houston  Sayreville Grand Haven  Sayreville  Grand Haven  Houston  Sayreville  BG  Sayreville  Sayreville  Sayreville  BG  Sayreville  Sayre		Grand Haven	BG OS MW	5 17 22	21-104 69-1000 16-125	52 154 129	36 221 144	0.65
Houston OS 68 1198-8963 4847 1569  Pinto Island BG 3 15-48 31 17  Grand Haven BG 5 39-1400 328 600  Sayreville BG 7 75-8550 3210 3453  Houston OS 67 10-1388 354 318  Pinto Island BG 3 38-1300 408 414	Chloride,	Sayreville	BG OS MW	6 29 20	70-1407 4511-11520 61-9572	403 8333 2150	520 2111 2250	<0.01
## Pinto Island BG 3 15-48 31 17 17 17 18 17 18 17 18 17 18 18 17 18 17 18 18 18 18 18 18 18 18 18 18 18 18 18	- /6	Houston	SO	89	1198-8963	4847	1569	•
Grand Haven     BG     5     39-1400     328     600       OS     24     9-1238     557     344     **       Sayreville     BG     7     75-8550     3210     3453       ate,     MW     23     225-2600     798     774       Houston     OS     67     10-1388     354     318       Pinto Island     BG     3     35-131     72     52       MW     19     38-1300     408     414		Pinto Island	BG OS MW	3 20	15-48 82-6514 24-625	31 2970 180	17 2706 175	<0.01
Ate, MW 23 75-8550 3210 3453 Ate, MW 23 225-2600 798 774 Houston OS 67 10-1388 354 318 Pinto Island BG 3 35-131 72 52 OS 29 170-2288 886 635 635 MW 19 38-1300 408 414		Grand Haven	BG OS	24 19	39-1400 9-1238 136-1900	328 557 825	600 344 571	<0.01
Houston OS 67 10-1388 354 318  Pinto Island BG 3 35-131 72 52  OS 29 170-2288 886 635  MW 19 38-1300 408 414	Sulfate,	Sayreville	BG OS MW	7 30 23	75-8550 313-4213 225-2600	3210 2818 798	3453 781 774	0.06
BG 3 35-131 72 52 OS 29 170-2288 886 635 MW 19 38-1300 408 414		Houston	SO	67	10-1388	354	318	
		Pinto Island	BG OS MW	3 29 19	35-131 170-2288 38-1300	72 886 408	52 635 414	<0.01

(Continued)

TABLE 22, (Continued)

Parameter	Site and Location	2 "	Number of Samples	Range	Mean	Standard Deviation	Probabilty p Value On-site vs. Off-site
	Grand Haven	BG OS MW	6 15 23	24-715 180-1127 ND-569	223 589 286	279 278 146	< 0.01
ALK, mg/l	Sayreville	BG OS MW	8 31 21	ND-10 4-672 ND-1276	2.5 196 259	4.6 219 400	0.45
	Houston	SO	89	250-2275	1092	538	ı
	Pinto Island	BG OS	3 29 19	40-120 48-1066 62-479	85 446 210	55 336 122	< 0.01
	Grand Haven	BG OS	6 24 19	30-345 35-610 20-160	102 244 87	126 173 48	< 0.01
TOC, mg/l	Sayreville	BG OS MW	8 32 23	ND-90 15-280 1-780	20 85 141	29 72 191	0.12
	Houston	SO	7.0	30-1190	304	278	
	Pinto Island	BG OS MW	2 29 16	10-20 5-310 2-110	15 73 29	73 25	0.03

TABLE 22. (Continued)

Parameter	Site and Location	ž	Number of Samples	Range	Mean	Standard Deviation	Probability p Value On-site vs. Off-site
	Grand Haven	BG OS	6 18 24	0.1-4 0.3-1.0 0.3-4	1.4	1.7	0.24
Cadmium,	Sayreville	BG OS MW	8 32 23	ND-147 1-203 ND-154	50 58 22	56 61 43	0.04
	Houston	SO	82		1.3	1.4	-
	Pinto Island	BG OS MW	3 40 26	ND-1.2 0.2-40 ND-5.3	0.57 2.7 0.59	0.60 6.5 1.1	0.24
	Grand Haven	BG OS MW	5 11 13	ND-0.03 ND-0.8 ND-0.03	0.015	0.014 0.04 0.014	•
Phosphate,	Sayreville	BG OS MW	6 23 18	ND-0.11 ND-0.02 ND-0.01	0.035	0.046	•
1/6w	Houston	SO	99	ND-6.95	0.11	0.17	
	Pinto Island	BG OS MW	10 7	0.002-0.08 0.005-0.5 0.004-0.09	0.032	0.038 0.147 0.049	•

(Continued)

TABLE 22. (Continued)

	Site and	Ž	Number of			Standard	Probability p Value
Parameter	Location		Samples	Range	Mean	Deviation	On-site vs. Off-site
	Grand Haven	BG	9	ND-412	170	160	
		SO	18	24-342	128	93	< 0.01
		MM	24	3092	27	23	
	Sayreville	BG	8	100-1790	515	544	
	•	SO	33	30-1200	420	322	0.01
Nickel,		MM	28	7-920	237	223	
mg/1	Houston	SO	82	2-1000	59	158	•
	Pinto Island	BG	е	ND-11	4	e	
		SO	40	2-300	42	99	0.02
		MM	26	2-40	10	6	
	Grand Haven	BG	9	0.01-5.9	1.91	2.35	
		SO	19	0.001-4.68	1.21	1.31	0.85
		MM	24	0.012-3.64	1.30	1.51	
	Sayreville	BG	æ	0.5-36	12	12	
Manganese,		SO	32	0.7-9	6.4	2.8	0.55
mg/ī		MM	28	0.6-22	7.4	8.6	
	Houston	SO	82	0.2-47.5	12.3	10.9	•
	Pinto Island	BG	3	0.0005-0.07	0.27	0.38	
		SO	40	0.066-68.2	9.1	15.2	0.01
		MM	26	0.0005-5.13	1.2	1.8	

TABLE 22 (Continued)

Parameter	Site and Location	ž	Number of Samples	Range	Mean	Standard Deviation	Probability p Value On-site vs. Off-site
	Grand Haven	BG OS	6 18 24	0.008-0.32 0-0.31 0.004-0.188	0.157 0.005 0.026	0.119 0.095 0.039	0.24
Iron, mg/l	Sayreville	BG OS MW	6 32 26	0.166-2500 0.011-49.6 0.004-71.6	538 3.5 3.7	988 12 14	6.0 <
,	Houston	SO	92	0.003-1.1	0.147	0.213	-
	Pinto Island	BG OS MW	3 40 26	0.015-0.07 0.003-0.8 0.002-0.52	0.038 0.054 0.078	0.029 0.131 0.131	0.45
Copper,	Grand Haven	BG OS	6 18 24	2-22 2-62 0.3-33	12 19 10	7 17 9	0.02
1/61	Sayreville	BG OS MW	3.2 2.8 2.8	20-11400 3-3000 1-6100	2616 231 500	3740 540 1400	0.3
	Houston	SO	82	3-165	56	29	•
	Pinto Island	BG OS	3 39 26	1-2 0.5-345 1-46	1 61 11	0.6 86 12	< 0.01

TABLE 22 (Continued)

Parameter	Site and Location	N S	Number of Samples	Range	Mean	Standard Deviation	Probability p Value On-site vs. Off-site
	Grand Haven	BG OS	6 18 24	0.030-0.640 0.001-0.230 0.002-0.126	0.176 0.037 0.053	0.235 0.058 0.075	0.45
Zinc,	Sayreville	BG OS MW	8 32 29	0.23-7.6 0.18-6.48 0.002-77.3	3.8 2.44 4.16	3.3 1.94 14	0.48
mg/1	Houston	BG	09	0.006-1.2	0.084	0.153	1
	Pinto Island	BG OS MW	3 40 25	0.021-0.030 0.002-3.22 0.007-0.24	0.024 0.60 0.072	0.005 0.91 0.065	<0.01
	Grand Haven	BG OS MW	6 10 11	0.3-1.1 0-1.0 0.1-0.9	0.63	0.29 0.36 0.27	×0.8
Mercury ug/l	Sayreville	BG OS MW	8 12 12	ND-0.32 ND-1.6 ND-9	0.13 0.34 0.34	0.14 0.45 0.31	% O .
	Houston	so	99	ND-3	0.48	0.31	•
	Pinto Island	BG OS	2 21 15	ND-0.2 ND-1.1 ND-0.8	0.1 0.34 0.28	0.34	0.53

TABLE 22 (Continued)

Parameter	Site and Location	ž	Number of Samples	Range	Mean	Standard Deviation	Probability p Value On-site vs. Off-site
	Grand Haven	BG OS	5 19 24	1 to 2 1 to 3 1 to 2		111	•
Lead,	Sayreville	BG OS MW	8 33 27	4-32 1-39 1-50	12 14 9	10 10	6.0 <
1/61	Houston	so	82	0.6-80	<b>&amp;</b>	11	
	Pinto Island	BG OS MW	3 40 26	0.5-2 0-6.4 0-5	1.1	0.77	0.8
Eh, mV	Grand Haven	BG OS MW	3 5 12	-75 to +70 43 to +300 -80 to +190	6 205 28	74 106 85	< 0.01
	Sayreville	BG OS MW	32 24	+210 to +380 -90 to +350 -120 to +180	280 131 52	70 126 112	0.02
	Houston	so	99	-100 to +200	24	8.5	•
	Pinto Island	BG OS MW	2 32 19	+90 to +210 -20 to +390 -83 to +270	166 163 149	59 100 95	0.63

TABLE 22. (Concluded)

Parameter	Site and Location	ž	Number of Samples	Range	Mean	Standard Deviation	Standard probability p Value Deviation On-site vs. Off-site
	Grand Haven	BG OS MW	5 8 12	6.2-7.3 5.8-7.7 6.1-7.3	6.7 6.6 6.8	0.4	0.35
Нq	Sayreville	BG OS	68 34 30	2.8-7.2 5.1-6.8 3.0-7.2	5.9	1.5 0.6 0.9	9.0
	Houston	SO	82	5.6-8.0	6.9	0.5	•
	Pinto Island	BG OS	3 38 24	6.1-8.2 4.8-8.0 5.7-8.2	7.2	4.0	0.1

TABLE 23. STATISTICAL CHARACTER OF GROUNDWATER

Parameter	Site and Location	ation	Number of Samples	Range	Mean	S. D.	Probabi BG vs. GW	Probability p Values vs. GW BG vs. US	is US vs. GW
Potassium, mg/l	Grand Haven	BG US GW	6 10 12	3-39 7-110 1-20	13 34 10	14 32 5	0.5	0.15	0.02*
	Sayreville	BG US GW	8 12 13	1-923 99-959 12.2-650	127 413 120	322 307 195	* 6.0 <	0.07*	0.015
	Pinto Island	BG US GW	3 16 17	1-3 17-200 3-165	2 108 31	1 55 40	0.27	< 0.01	< 0.01*
Sodium, mg/l	Grand Haven	BG US GW	6 11 12	9-20 31-680 6075	13 114 40	4 188 18	< 0.01	0.2	0.18
	Sayreville	BG US GW	8 12 12	25-1700 2770-6200 30-2670	520 4025 841	597 925 765	0.33*	< 0.01*	< 0.01*
	Pinto Island	BG US GW	3 16 17	5-30 20-5800 2-1061	14 2121 198	14 1459 260	0.25	0.01*	< 0.01
Calcium, mg/l	Grand Haven	BG US GW	111	7-560 50-480 170-530	188 261 331	252 161 107	0.12	0.5*	0.23*
	Sayreville	BG US GW	8 12 12	2-140 92-670 170-530	27 300 331	47 187 107	0.15	< 0.01	< 0.01*
	Pinto Island	BG US GW	3 16 15	31-81 29-350 8-166	56 173 72 (Continued)	25 108 47	0.45	0.01*	0.01

TABLE 23. (Continued)

Parameter	Site and Location	ation	Number of Samples	Range	Mean	S.D.	Probe BG vs. GW	Probability p Values GW BG vs. US US	lues US vs. GW	1
Magnesium, mg/l	Grand Haven	BG US GW	6 11 12	8-75 20-93 13-65	31 66 43	26 21 15	0.35*	0.02*	0.01	1
	Sayreville	BG US GW	8 12 13	3-362 440-1050 7-504	98 651 170	117 175 184	0.28*	<0.01*	<0.01*	
	Pinto Island	BG US GW	3 16 17	1-40 12-550 2-140	14 237 39	22 161 48	0.2*	0.04	<0.01	
Sufate, mg/l	Grand Haven	BG US GW	5 11 10	39-1400 9-1115 136-1700	328 417 743	600 306 591	0.22*	0.68	0.12	
	Sayreville	BG US GW	7 13 10	70-1407 4819-12188 61-2059	403 8226 971	520 1785 814	0.12	0.01	<0.01*	
	Pinto Island	BG US GW	5 11 12	21-104 64-1051 40-109	52 185 91	36 289 27	0.08	0.15	0.25	
Alkalinity	Grand Haven	BG US GW	6 10 12	24-715 264-1120 141-569	223 734 326	279 330 142	0.31	<0.01*	<0.01	
	Sayreville	BG US GW	8 10 7	ND-10 48-816 24-343	2.5 360 104	4.6 271 129	0.04	<0.01	0.04	
	Pinto Island	BG US GW	3 16 14	40-120 45-977 62-479	85 484 230	55 290 126	0.07	0.015*	<0.01	
				(Continued)	(penu					

TABLE 23. (Continued)

Parameter	Site and Location	tion	Number of Samples	Range	Mean	s.b.	BG vs. 0	Probability p Values GW BG vs. US vs	p Values US US vs. GW	
Total organic carbon	Grand Haven	BC US GW	9 10	30-345 50-370 30-160	102 211 89	126 103 46	0.75	0.12*	<0.01	
	Sayreville	BG US GW	8 13 10	ND-90 15-490 1-165	20 191 49	29 161 60	0.24	<0.01	0.02	
	Pinto Island	BG US GW	2 15 13	10-20 0-240 2-235	15 79 53	7 67 63	0.07*	<0.01*	0.3*	
Cadmium, ug/l	Grand Haven	BG US GW	111	0.3-4 0.7-1.0 0.3-2	1.4 0.79 0.92	0.44	0.35	0.20	0.49*	
	Sayreville	BG US GW	8 12 12	ND-147 ND-129 ND-154	50 22 43	39 60	*8.0	0.23*	0.32*	
	Pinto Island	BG US GW	3 16 17	ND-1.2 0.1-46 ND-5.3	0.57	0.60	0.86	09.0	0.30	
Nickel, mg/l	Grand Haven	BG US GW	6 11 12	ND-412 1-190 7-77	170 65 22	164 59 20	<0.01	0.07	0.03	
	Sayreville	BG	8 112 113	80-1790 30-890 8-490	515 325 237	545 292 172	0.1	0.3	0.38	
	Pinto Island	BG US GW	3 16 17	ND-11 3-270 ND-40	4.3 40 11	5.9 67 10	0.18*	0.27	0.1	
				(Continued)	ed)					

TABLE 23. (Continued)

Parameter	Site and Location	tion	Number of Samples	Range	Mean	S.D.	Probe BG vs. GW	Probability p Values GW BG vs. Us US	vs.	GW
Manganese, mg/l	Grand Haven	BG US GW	6 10 12	0.5-5.9 0.002-2.7 0.016-4.8	1.91 0.76 1.50	2.35 0.90 1.69	0.75*	0.19	0.4*	
	Sayreville	BG US GW	8 12 12	0.5-36 1.3-16.2 1.1-20	12 6 8	12 4 7	0.35	0.12	4.0	
	Pinto Island	BG US GW	3 16 17	0.0005-0.07 0.4-53.6 0.001-4.5	0.027 17 1.2	0.038 14.6 1.7	0.25	0.25	<0.01	
Iron, mg/l	Grand Haven	BG US GW	11 12	0.008-0.320 ND-0.830 0.008-0.045	0.157 0.125 0.018	0.119	<0.01	0.75*	0.15	
	Sayreville	BG US GW	8 12 12	0.5-36 1.3-16.2 1.1-20	12 6 8	12 4 7	0.35	0.12	0.4	
	Pinto Island	BG US GW	3 16 17	0.015-0.070 0.003-0.210 0.002-0.510	0.038	0.029	0.5*	0.75*	0.08*	
Copper, ug/l	Grand Haven	BG US GW	6 11 12	2-22 1-59 0.3-12	12 15 6	7 18 4	*60.0	7.0	0.1	
	Sayreville	BG US GW	8 12 12	20-11400 3-2050 1-6100	2616 321 1035	3740 673 2055	0.23	0.05	0.31	
	Pinto Island	BG US GW	3 16 17	1-2 1-225 1-33	1 41 9.9	0.6 54 9.5	0.13	0.25	0.02	
				(Cont	(Continued)					

TABLE 23. (Continued)

Parameter	Site and Location		Number of Samples	Range	Mean	S.D.	BG vs.	Probability p Values GW BG vs. US US v	ty p Versions		GW
Zinc, mg/l	Grand Haven BG US GW	2003	6 11 12	0.030-0.640 0.001-0.080 0.002-0.126	0.176 0.019 0.032	0.235 0.022 0.042	0.05	0.03	33	0.32	
	Sayreville BG US GW	0 to 3	8 12 14	0.23-7.6 0.14-4.16 0.002-77.3	3.8	3.3 1 20	0.59	0.01	11	0.24	
	Pinto Island BG US GW	0 W 3	3 16 17	0.021-0.030 0.006-3.51 0.008-0.24	0.024 0.41 0-073	0.005	6.0	<0.01	11	0.15	
Mercury, ug/l	Grand Haven BG US GW	2 w 3	277	$0.3-1.1 \\ 0-1.0 \\ 0.1-0.9$	0.64	0.32 0.37 0.28	6.04	0.0		0.87	
	Sayreville BG US GW	2 w 2	8 9 11	0-032 0.08-1.6 0.004-0.68	0.13 0.37 0.33	0.14	0.36	0.28	28	6.0	
	Pinto Island BC	BG US GW	8 8 7	ND-0.2 ND-1.0 ND-0.6	0.1	0.3	ı	•		×0.9	
Lead, ug/l	Grand Haven BC US	BG US GW	8 7 5	1-20 1-30	7 8 1	11 0	0.05	0.86	98	0.1	
	Sayreville B(US)	BG US GW	8 12 12	4-32 1-34 1-16	12 18 5	10 11 5	0.07	0.25	25	<0.01	
	Pinto Island B	BG US GW	3 16 17	0.5-2 ND-3.7 ND-5	1.1	0.77	0.39		69.0	°0°	

TABLE 23. (Concluded)

Parameter	Site and Location		Number of Samples	Range	Mean	S.D.	Probab BG vs. GW	Probability p Values GW BG vs. US US	ues US vs. GW
Chloride, mg/1	Grand Haven	BG US GW	5 11 12	21-104 64-1051 40-109	52 185 91	36 289 27	0.08*	0.15	0.25
	Sayreville I	BG US GW	7 13 10	70-1407 4819-12188 61-2059	403 8226 971	520 1785 814	0.12*	<0.01	<0.01
	Pinto Island	BG US GW	3 16 15	15-48 16-9224 24-1153	31 3193 238	17 2524 309	0.25	0.05	<0.01
Hd	Grand Haven	BG US GW	6 5 5	6.2-7.3 6.3-7.2 6.4-7.3	6.9	444	1	ı	1
	Sayreville E	BG US GW	8 13 14	2.8-7.2 4.1-6.7 4.2-6.8	3.9	1.5		1	·
	Pinto Island E	BG US GW	3 16 17	6.1-8.2 5.6-8.3 5.7-8.2	7.2	0.4	1	1	1
Eh, mV	Grand Haven	BG US GW	m 0, 9	-75 to 70 90 to 140 2 to 190	6 115 39	74 35 83	1	ı	1
	Sayreville F	BG US GW	6 9 12	210 to 380 6 to 290 61 to 230	280 112 136	70 85 62	•		ı
	Pinto Island E	BG US GW	2 12 13	90 to 210 -31 to +300 -3 to +270	166 129 158	85 84	t	1	ı
Legend: BG: US:	Background sample Under-site sample	e GW: e ND:		Monitoring well sample Not detected	sp sp	Samples from special "t"	from two populations, "t" test applied (for details see	ions, (for detail	ls see

TABLE 24. IMPORTANT SOLUBILITY PRODUCTS (Ksp) OF TRACE METALS\*

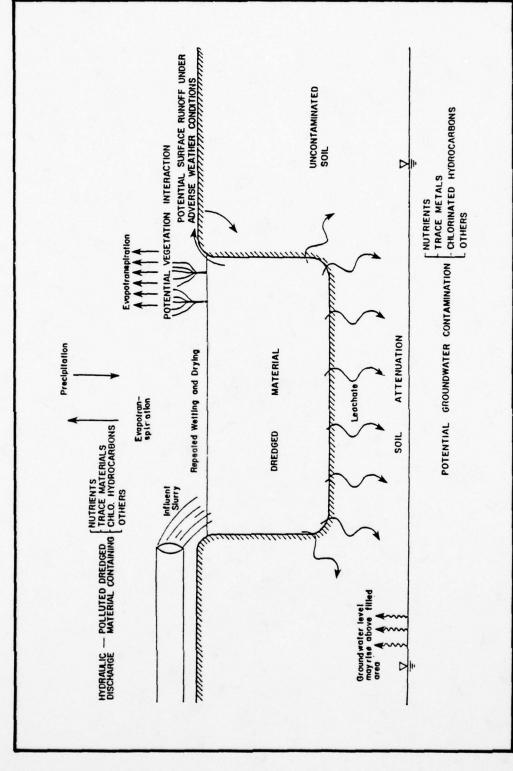
Metal	Oxide	Hydroxide	Carbonate	Sulfide	Chloride	Phosphate	Silcate
cd(II)		13.6	13.6	26.1			
Ca(II)		5.26	8.32 (calcite), 8.22 (argonite), 16.7** (dolomite)	2.94		6.25 (CaHOP <sub>4</sub> ) 26 (Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ) 1.14 (CaH <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> ) 6.4 (CaHPO <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ) 40.9 (Ca <sub>4</sub> H (PO <sub>4</sub> ) <sub>3</sub> ) 44.6 (Ca <sub>5</sub> OH (PO <sub>4</sub> ) <sub>3</sub> ) 120.8 (Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> ;	morillonite)
Cu(II)	20.4	18.6	9.63 (CuCO <sub>3</sub> ), 33.2 (Cu <sub>2</sub> Co <sub>3</sub> (OH) <sub>2</sub> )	35.2		37.7	
Fe(II)		15.3	10.2	16.9(FeS)		33.3	18.9**
FellII	) 80** (Fe <sub>2</sub> O <sub>3</sub> )	39.3		18.2 (Fe <sub>3</sub> S <sub>4</sub> )		25.8	
Pb(II)	15.4 (PbO)	16.1 18.8 (Pb <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> )	13.1	26.6	4.79	43.5, 12.6** (PhHPO <sub>4</sub> )	
Mn(II)		9.2 (active) 11.6 (brucite)	4.9 (magnesite), 5.4 (nesquehonite 16.7 (MgCa(CO <sub>3</sub> ) <sup>**</sup> <sub>2</sub>	e),	4.44** (MgCl <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ), 4** (KMgCl <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub> )	28.4 (Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> )  12.6** (mgNH <sub>4</sub> (PO <sub>4</sub> ) 13.2** (MgNH <sub>4</sub> PO <sub>4</sub> (H <sub>2</sub> O)	120)6

(Continued)

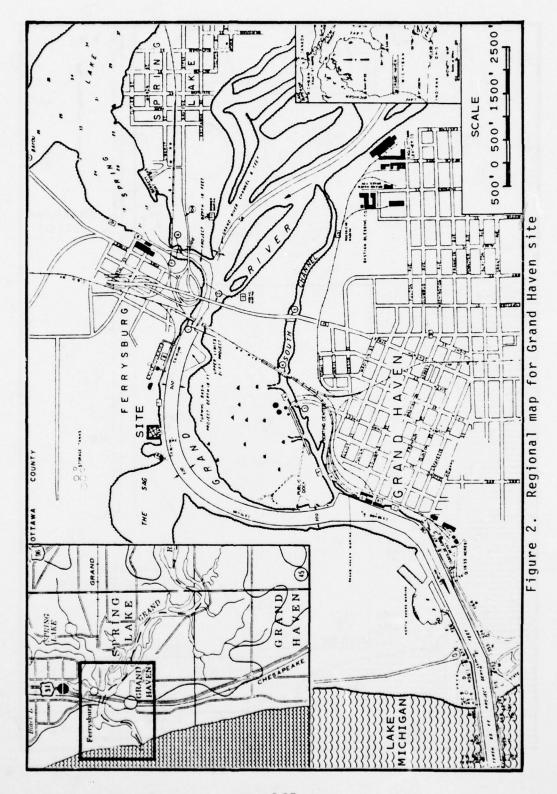
TABLE 24. (Continued)

Metal	Oxide	Hydroxide	Carbonate	Sulfide	Chloride	Phosphate	Silcate
Mn(II)	0.92**	12.7	9.3	12.9		22	13.2**
				(crystalin	ne),		
				15.7			
				(precipita	a-		
				tated)			
77(II)	25.7**	25.4		52.2	13.8		
				(meta-			
				cinnabar)			
				53.6			
				(cinnabar)			
K(I)			-4.11				76★★
							(orthoclase
							124**
							(muscovite
Na (1)							40.6**
							(albite)
							294**
							(Na-montmo
Ni(II)	1	4.81	18	1.5(a)			illonite)
	(	fresh)		5.7(β)			
	1	7.31					
	(	aged)					
Zn(II)	1	5.7(Amor- 10.	8 25	. 2	36.7	2	1.03**
	pl	hous),		hal-			
	19	6 (Amor-		ite),			
	pl	hous,	22	. 8			
	ag	ged), 16.9	(wu	rzite),			
	(0	cryst. aged)	22	.1 (pre-			
			cip	itated)			

\*\*NaAlSi $_30_8$ (s,albite) + 7H<sub>2</sub>0 + H<sup>+</sup> = Al<sup>3+</sup> + Ha<sup>+</sup> + 3H<sub>4</sub>SiO<sub>4</sub> + 30H<sup>7</sup>; CaAl $_2$ Si $_2$ O<sub>8</sub>(s,anorthite) + 8H<sub>2</sub>0 = 2Al<sup>3+</sup> + 2H<sub>4</sub>SiO<sub>4</sub> + 80H<sup>7</sup> + Ca<sup>2+</sup>; 1 1/2 KAlSi $_3$ O<sub>8</sub>(s,orthoclase) + 12H<sub>2</sub>0 = 1 1/2 Al<sup>3+</sup> + 1 1/2 K<sup>+</sup> + 4 1/2 H<sub>4</sub>SiO<sub>4</sub> + 60H<sup>7</sup>; KAl $_3$ Si $_3$ O<sub>10</sub>(0H)<sub>2</sub>(s,muscovite) + 10H<sub>2</sub>0 = 3Al<sup>3</sup> + K<sup>+</sup> + 3H<sub>4</sub>SiO<sub>4</sub> + 100H<sup>7</sup>; 3Na<sub>0.33</sub>Al<sub>2.33</sub>Si<sub>3.67</sub>O<sub>10</sub>(0H)<sub>2</sub>(s,Na-montmorillonite) + 30H<sub>2</sub>0 = 7Al<sup>3+</sup> + 11H<sub>4</sub>SiO<sub>4</sub> + 220H<sup>7</sup> + Na<sup>+</sup>; 3Ca<sub>0.33</sub>Al<sub>4.67</sub>Si<sub>7.33</sub>O<sub>20</sub>(0H)<sub>4</sub>(s,Ca-montmorillonite) + 60H<sub>2</sub>0 = 14Al<sup>3+</sup> + 22H<sub>4</sub>SiO<sub>4</sub> + 440H<sup>7</sup> + Ca<sup>2+</sup>; CaMg(CO<sub>3</sub>)<sub>2</sub>(s,dolonite) = Ca<sup>2+</sup> + Mg<sup>2+</sup> + 2CO<sub>3</sub><sup>2-</sup>; \*Values in p $^{K}$ sp (log  $K_{\mathrm{Sp}}$ ) when I (lonic temperature) = 0, T (temperature) = 25°C.  $\begin{aligned} \mathsf{MqIIII}_{\mathsf{q}}(\mathsf{PQ}_{\mathsf{q}})(s) &= \mathsf{M}_{\mathsf{q}}^{2^{+}} + \mathsf{NII}_{\mathsf{q}}^{4} + \mathsf{PQ}_{\mathsf{q}}^{3^{-}}; \\ \mathsf{MqIIII}_{\mathsf{q}}(\mathsf{PQ}_{\mathsf{q}})(\mathsf{II}_{\mathsf{2}}\mathsf{O})_{\mathsf{q}}(s) &= \mathsf{Mg}^{2^{+}} + \mathsf{NIII}_{\mathsf{q}}^{4} + \mathsf{PQ}_{\mathsf{q}}^{3^{-}} + \mathsf{6II}_{\mathsf{2}}^{\mathsf{O}}; \\ \mathsf{Mq}_{\mathsf{IIPO}\mathsf{q}}(\mathsf{H}_{\mathsf{2}}\mathsf{O})_{\mathsf{3}}(s) &= \mathsf{Mg}^{2^{+}} + \mathsf{IIPO}_{\mathsf{q}}^{4^{-}} + \mathsf{3II}_{\mathsf{2}}^{\mathsf{O}}; \\ \mathsf{MgCI}_{\mathsf{3}}(\mathsf{H}_{\mathsf{2}}\mathsf{O})_{\mathsf{q}}(s,\mathsf{bischofite}) &= \mathsf{Mg}^{2^{+}} + \mathsf{2CI}^{-} + \mathsf{6H}_{\mathsf{2}}^{\mathsf{O}}; \\ \mathsf{KMgCI}_{\mathsf{3}}(\mathsf{H}_{\mathsf{2}}\mathsf{O})_{\mathsf{3}}(s,\mathsf{carnallite}) &= \mathsf{K}^{+} + \mathsf{Mg}^{2^{+}} + \mathsf{3CI}^{-} + \mathsf{3H}_{\mathsf{2}}^{\mathsf{O}}; \\ \mathsf{NnO}_{\mathsf{2}}(s) &+ \mathsf{2II}^{+} &= \mathsf{Mn}^{2^{+}} + \mathsf{1/2} \; O_{\mathsf{2}} + \mathsf{II}_{\mathsf{2}}^{\mathsf{O}}; \\ \mathsf{MnSiO}_{\mathsf{3}}(s) &+ \mathsf{H}_{\mathsf{2}}\mathsf{O} &= \mathsf{Mn}^{2^{+}} + \mathsf{2OII}^{-} + \mathsf{SiO}_{\mathsf{2}}^{\mathsf{C}}(s); \\ \mathsf{IIgO}(s) &+ \mathsf{H}_{\mathsf{2}}\mathsf{O} &= \mathsf{Hg}^{2^{+}} + \mathsf{2OII}^{-}; \end{aligned}$  $Fe_2O_3(s) + 31_2O = 2Fe^{34} + 60H^{-};$   $Fe_2O_3(s) + 4_2O = Fe^{24} + 20H^{-} + 510_2(s);$   $Pb_3(0H)_2(CO_3)_2(s) = 3Pb^{24} + 20H^{-} + 2CO_3^{2};$   $PbO(s) + 11_2O = Pb^{24} + 20H^{-};$   $PbHPO_4(s) = Pb^{24} + 1PO_4^{2};$  $2n5i0_3(s) + 11_20 = 2n^{2+} + 2011^- + 5i0_2(s)$  FIGURES 1-78



Conception of land disposal of dredged material and associated problems Figure 1.



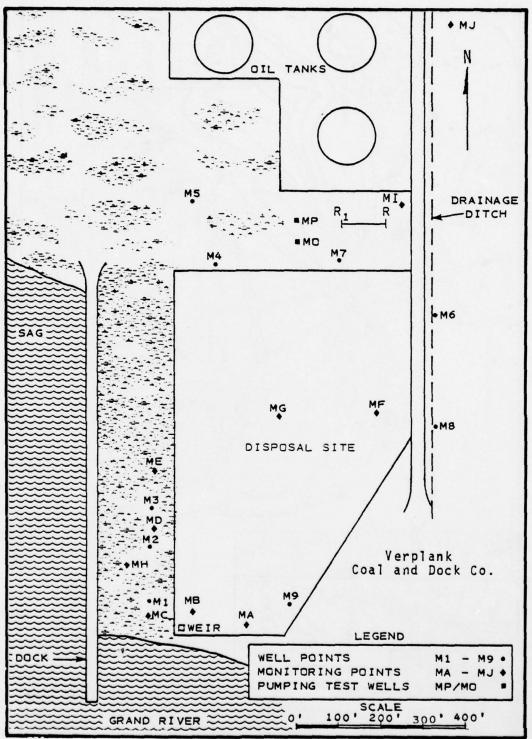


Figure 3. Grand Haven site

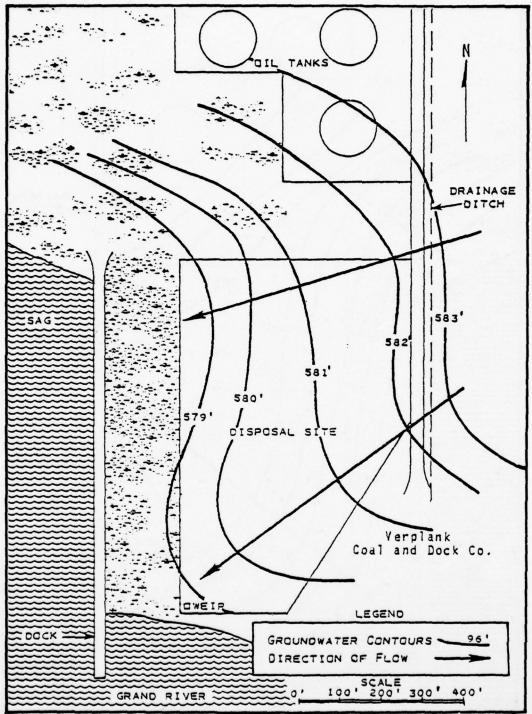


Figure 4. Water level contours on November 2, 1976, Grand Haven site

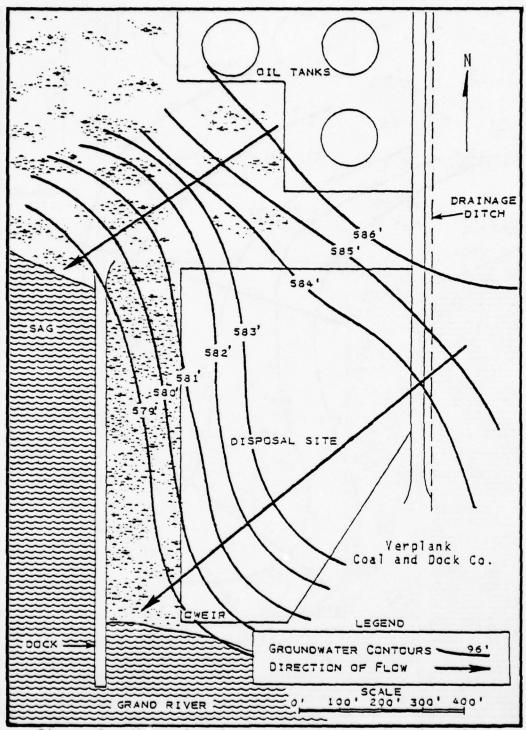


Figure 5. Water level contours on December 4, 1976, Grand Haven site

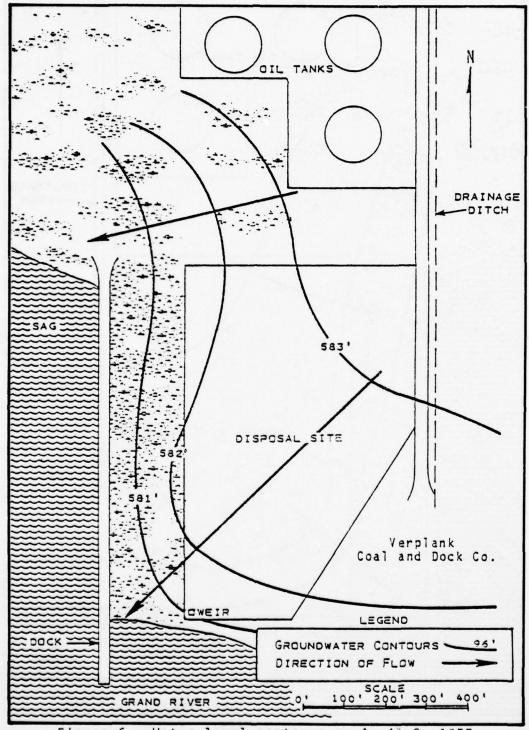


Figure 6. Water level contours on April 8, 1977, Grand Haven site

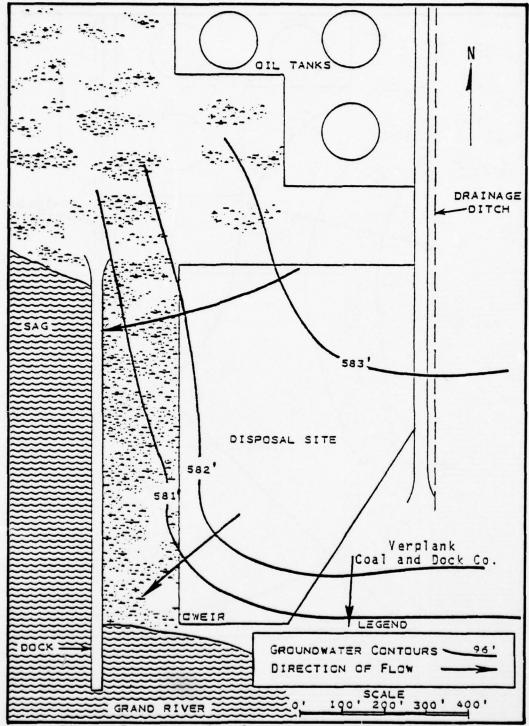


Figure 7. Water level contours on May 30, 1977, Grand Haven site

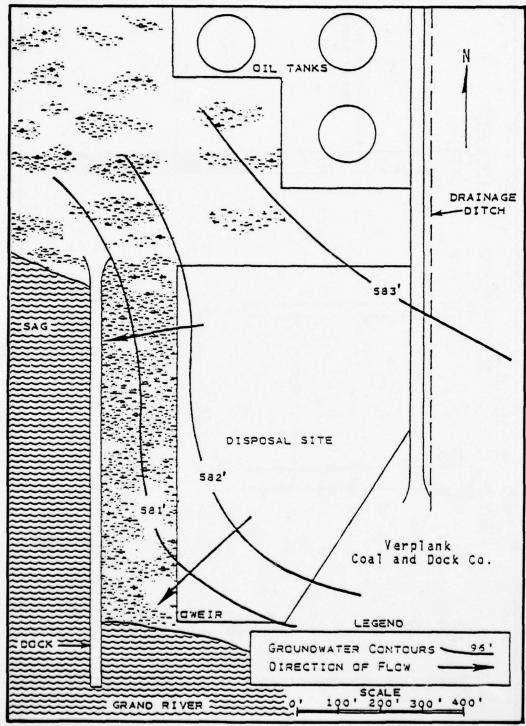


Figure 8. Water level contours on August 5, 1977, Grand Haven site

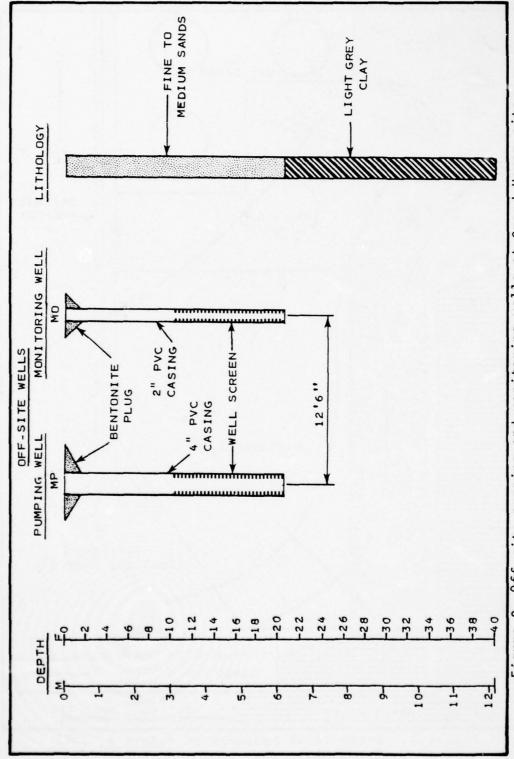
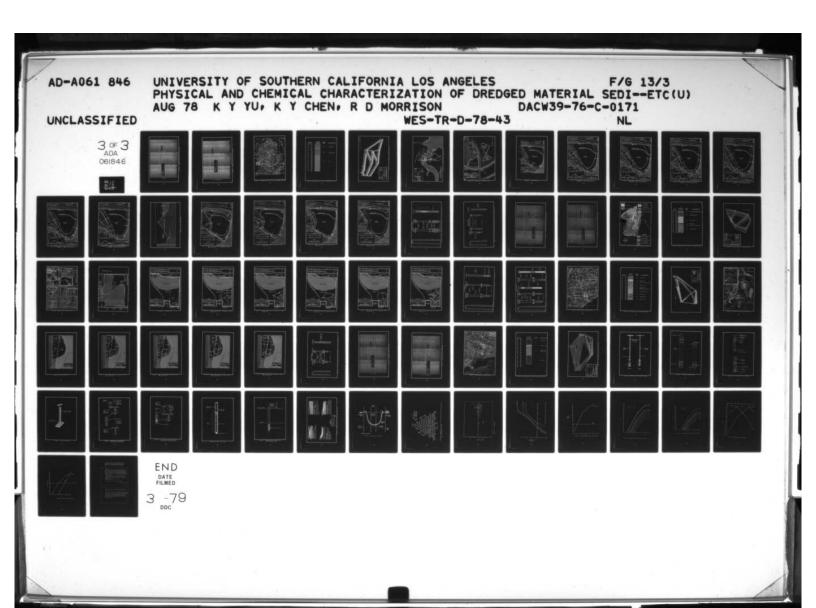
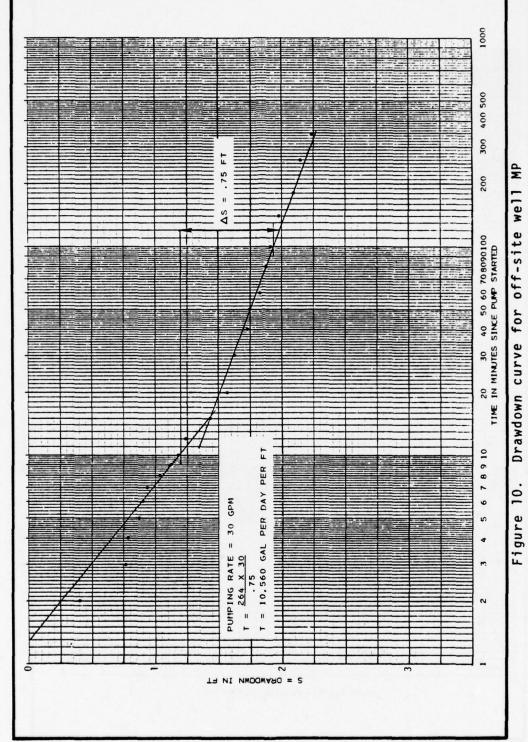
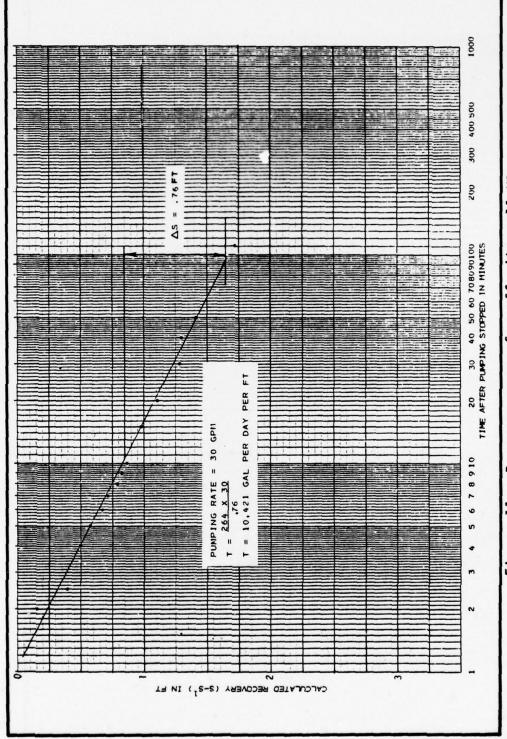


Figure 9. Off-site pumping and monitoring wells at Grand Haven site







igure 11. Recovery curve for off-site well MP



Figure 12. Geological map for central and southern Michigan

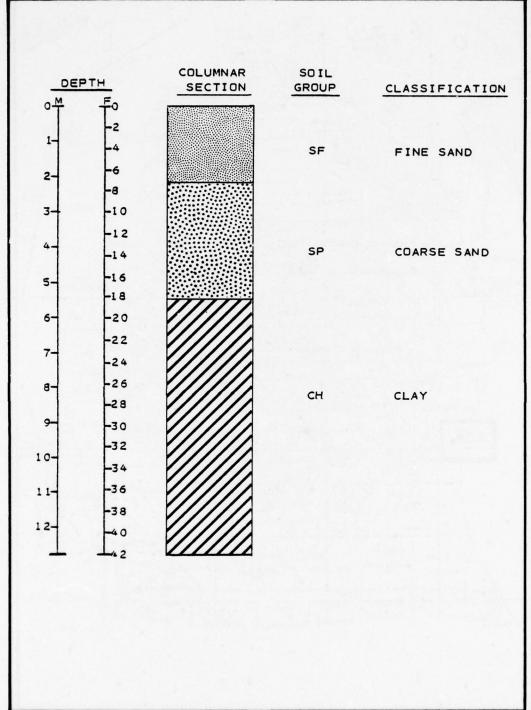
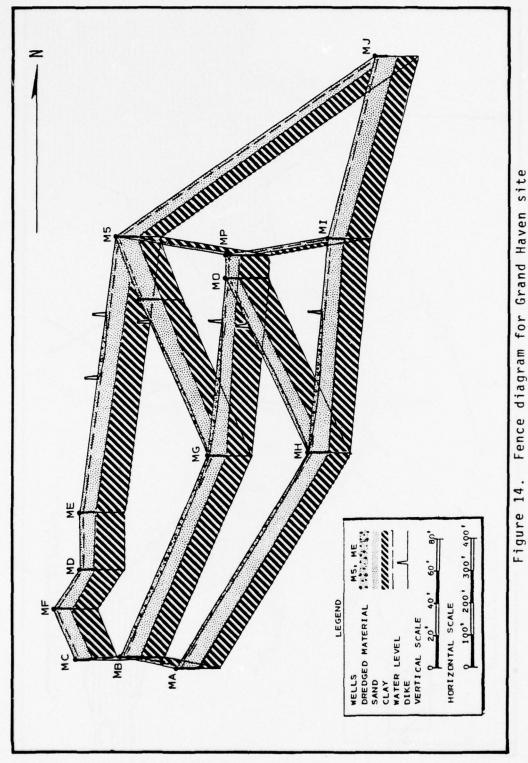
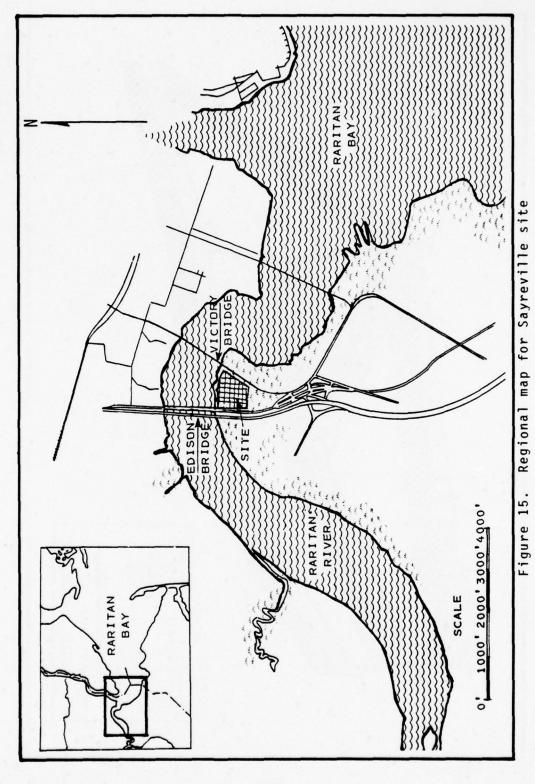


Figure 13. Generalized soil profile, Grand Haven site





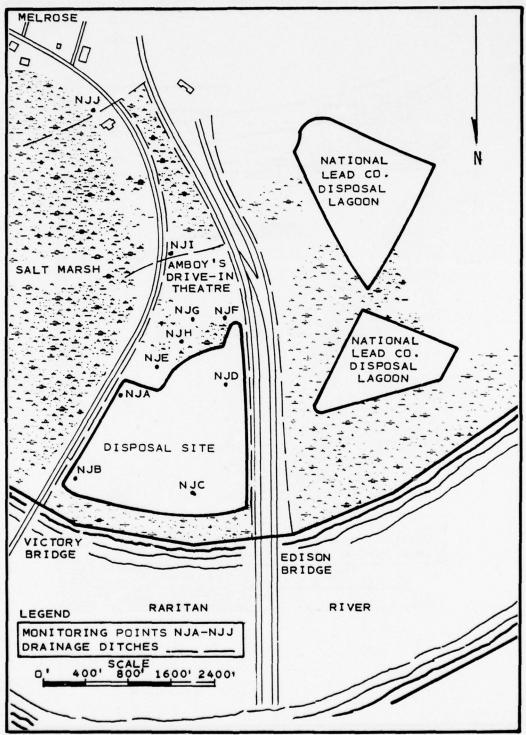


Figure 16. Area map for Sayreville site

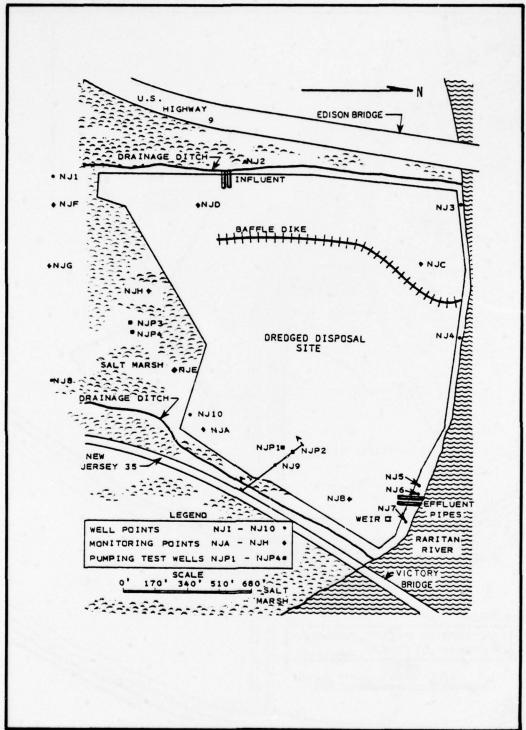


Figure 17. Sayreville site

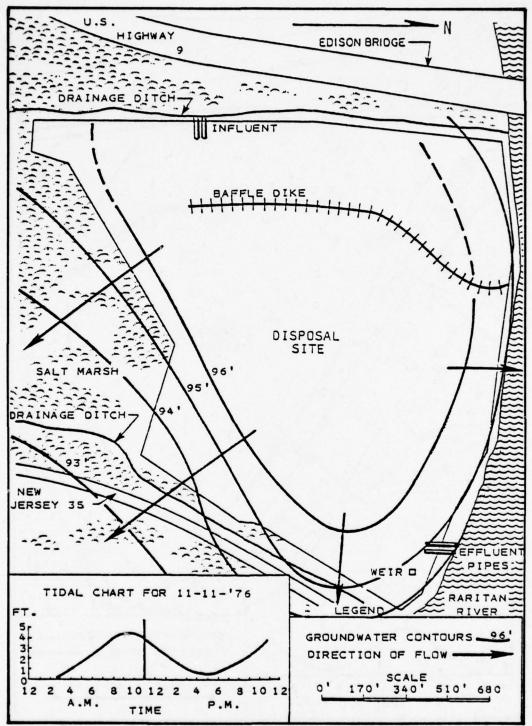


Figure 18. Groundwater contours at 11:00 a.m., November 11, 1976, Sayreville site

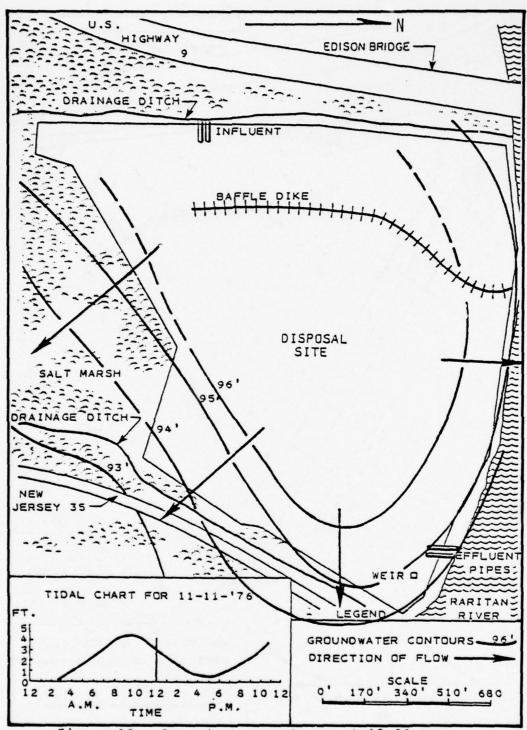


Figure 19. Groundwater contours at 12:00 p.m., November 11, 1976, Sayreville site

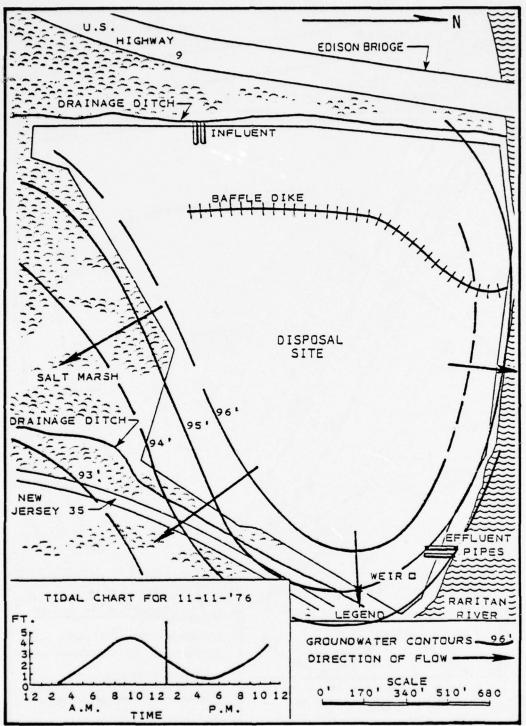


Figure 20. Groundwater contours at 1:00 p.m., November 11, 1976, Sayreville site

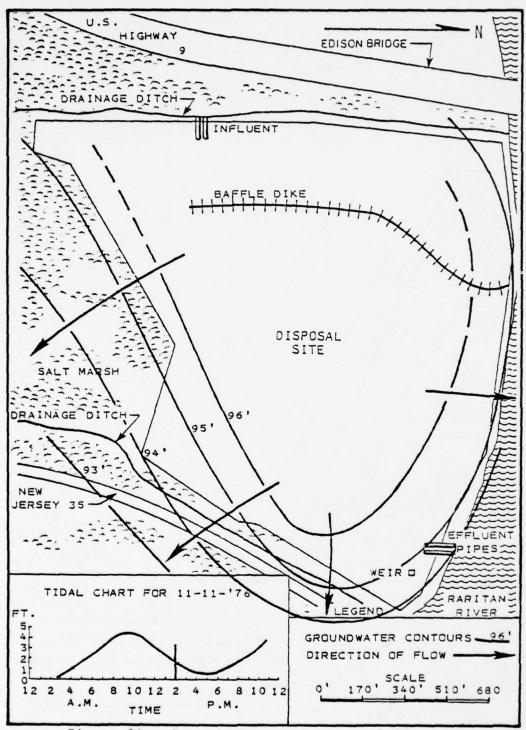


Figure 21. Groundwater contours at 2:00 p.m., November 11, 1976, Sayreville site

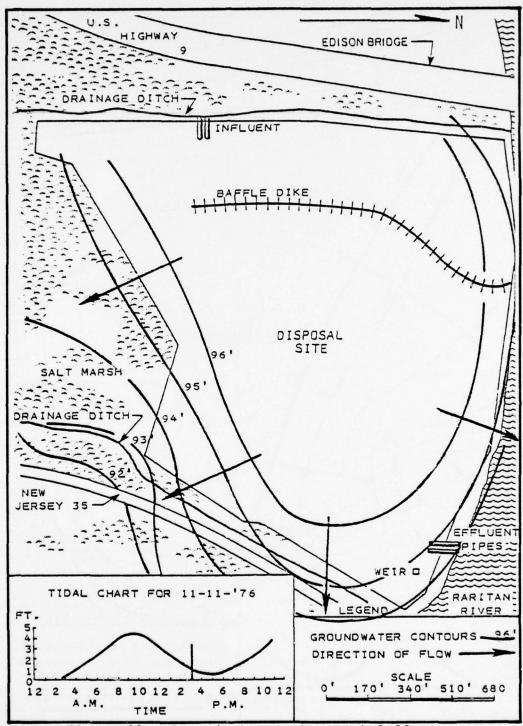


Figure 22. Groundwater contours at 3:00 p.m., November 11, 1976, Sayreville site

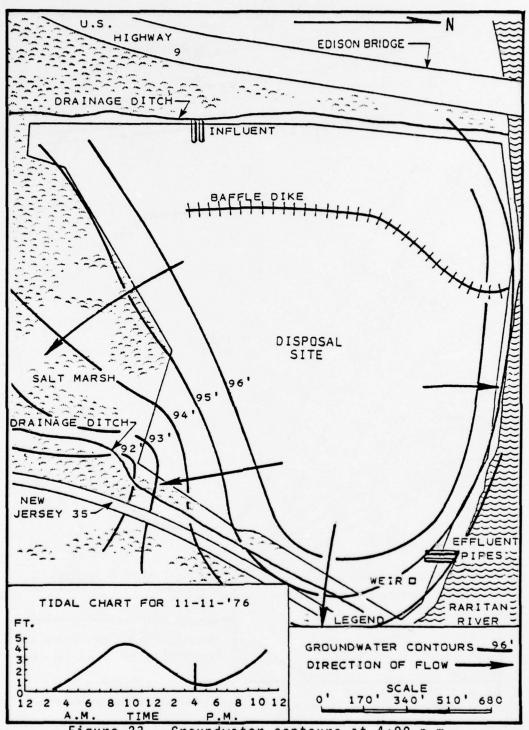
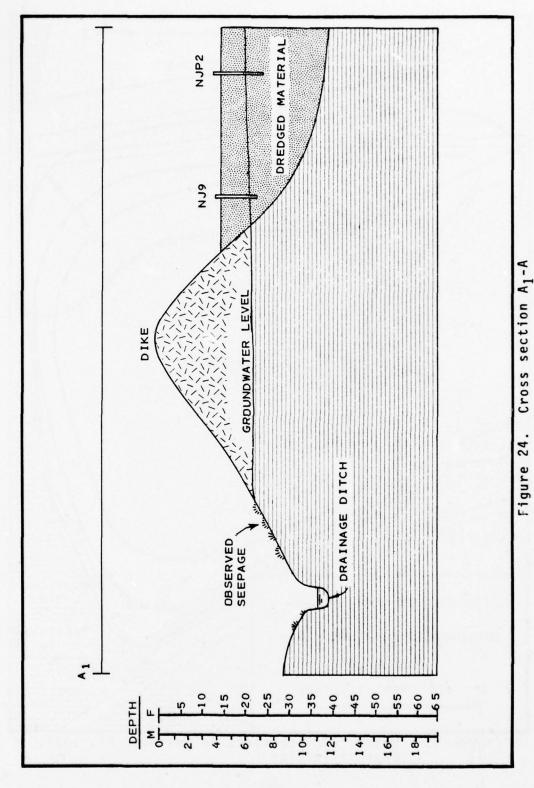


Figure 23. Groundwater contours at 4:00 p.m., November 11, 1976, Sayreville site



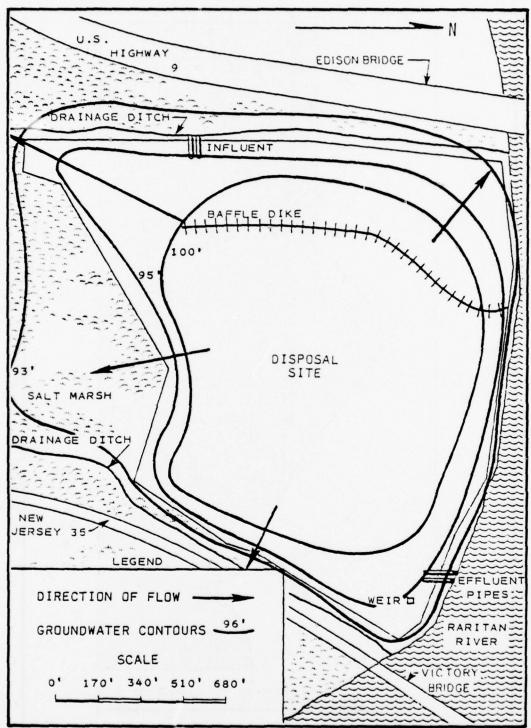


Figure 25. Water level contours on November 28, 1976, Sayreville site

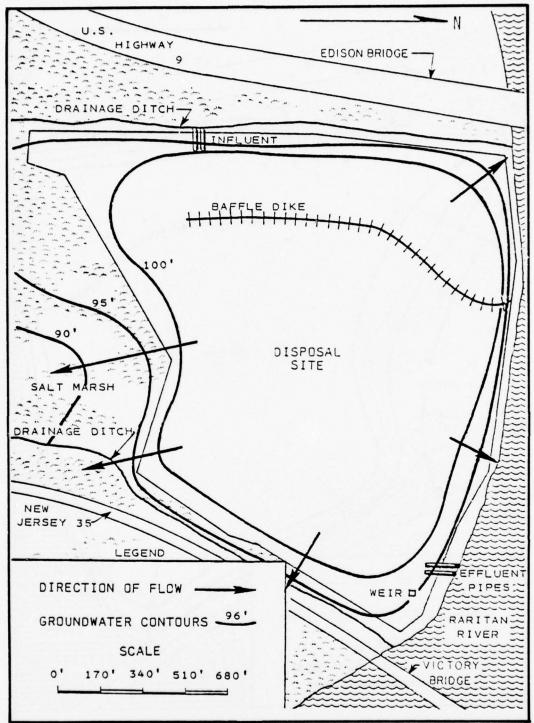


Figure 26. Water level contours on April 6, 1977, Sayreville site

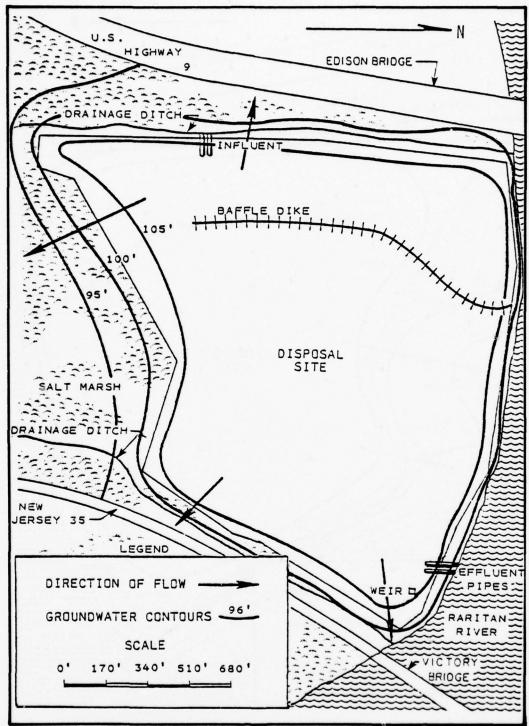


Figure 27. Water level contours on June 2, 1977, Sayreville site

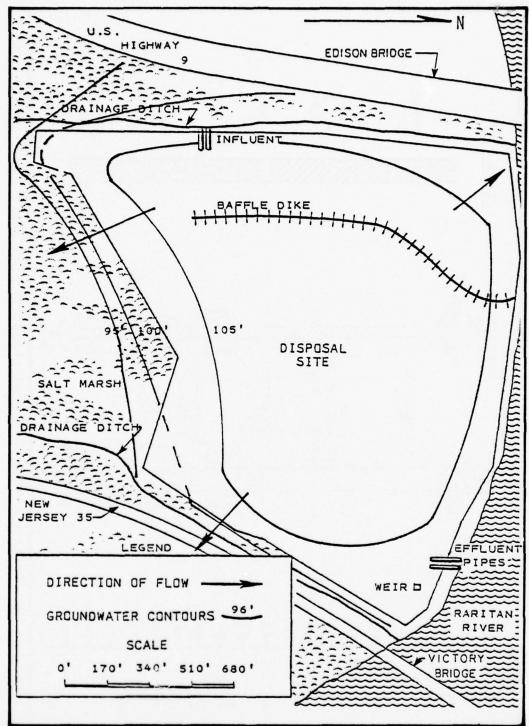
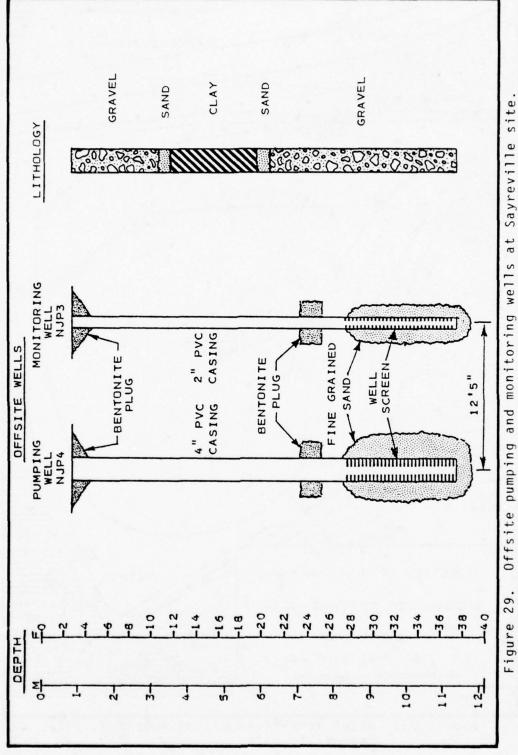
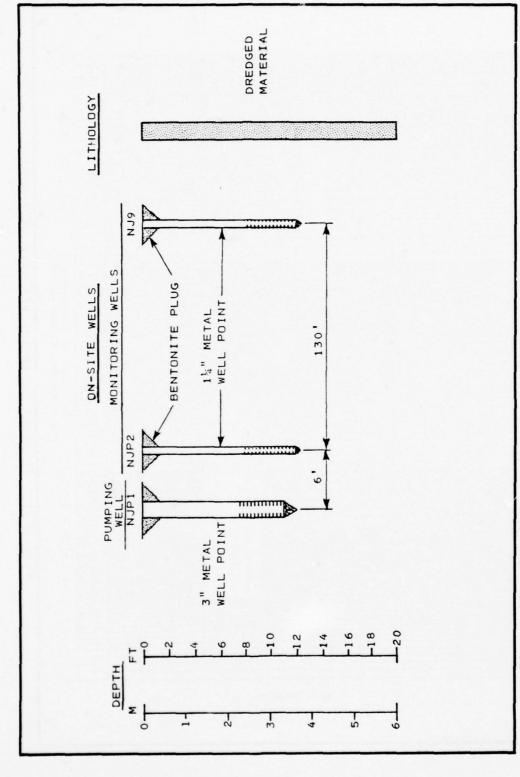


Figure 28. Water level contours on August 3, 1977, Sayreville site





On-site pumping and monitoring wells at Sayreville site Figure 30.

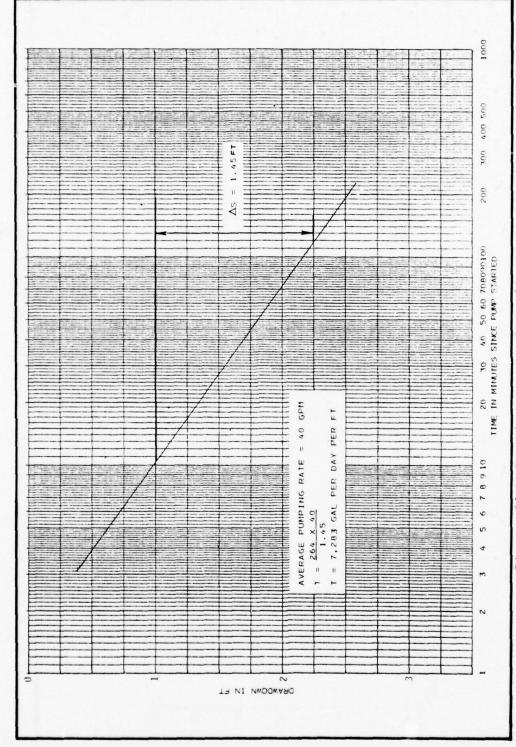


Figure 31. Drawdown curve for off-site well NJP4

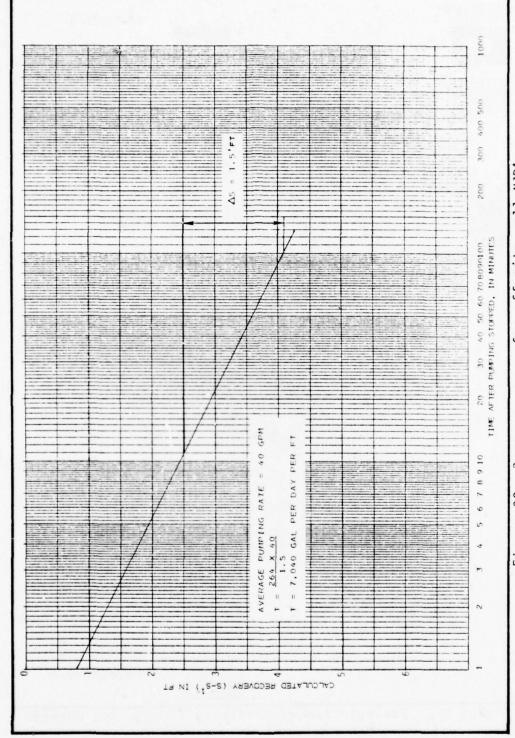


Figure 32. Recovery curvefor off-site well NJP4

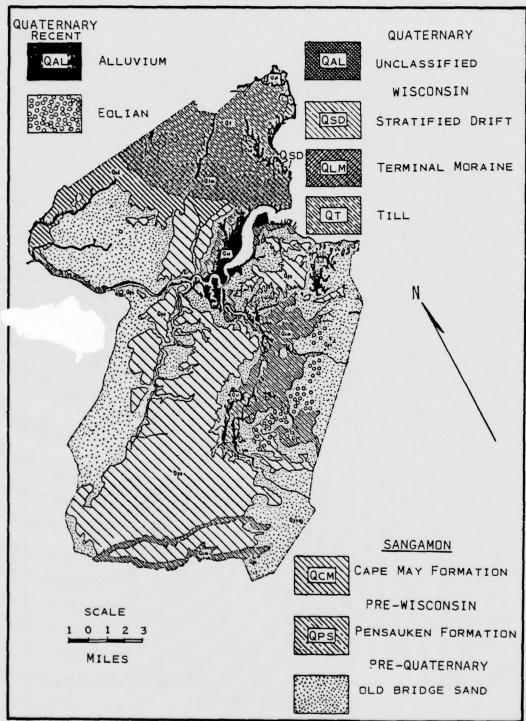


Figure 33. Geologic map of Middlesex County, New Jersey

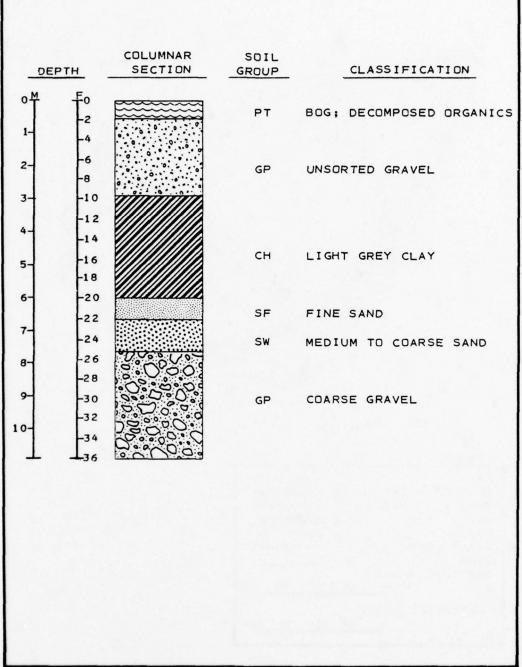


Figure 34 Generalized soil profile for Sayreville site

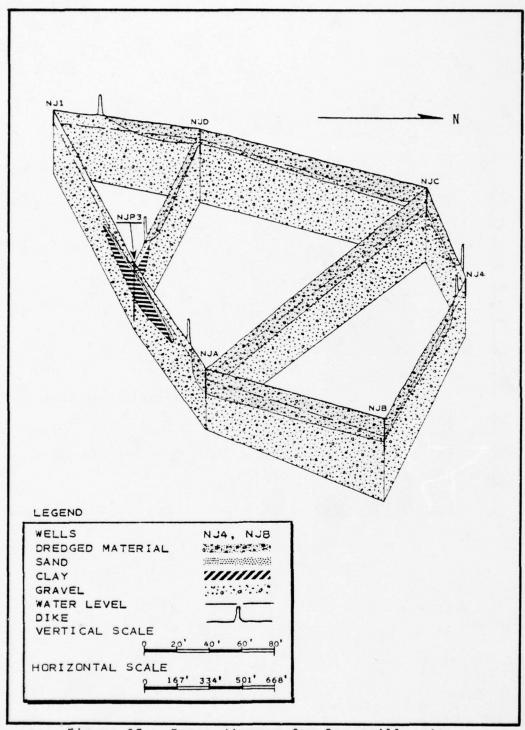


Figure 35. Fence diagram for Sayreville site

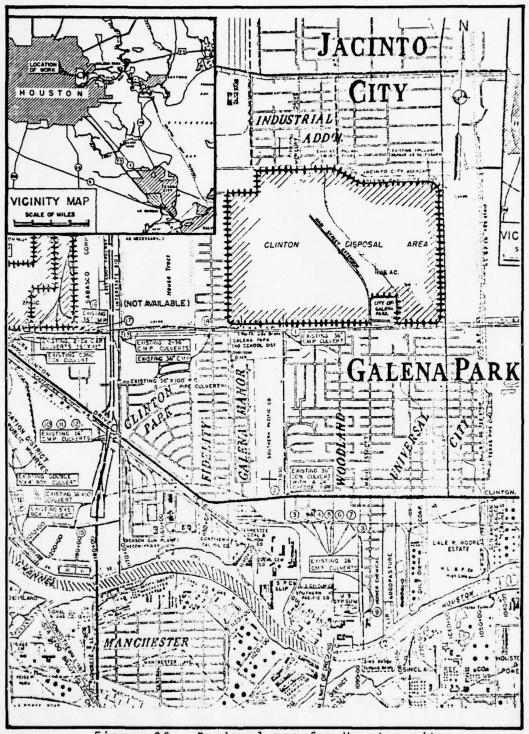
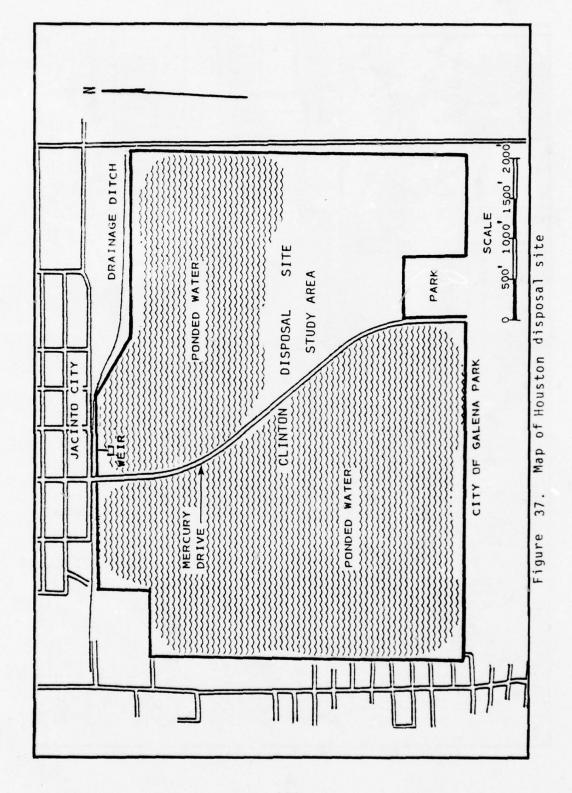


Figure 36. Regional map for Houston site



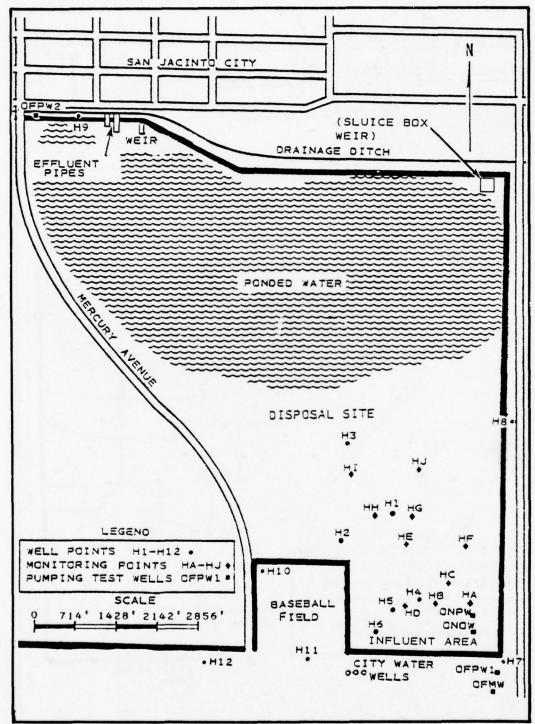


Figure 38. Houston site

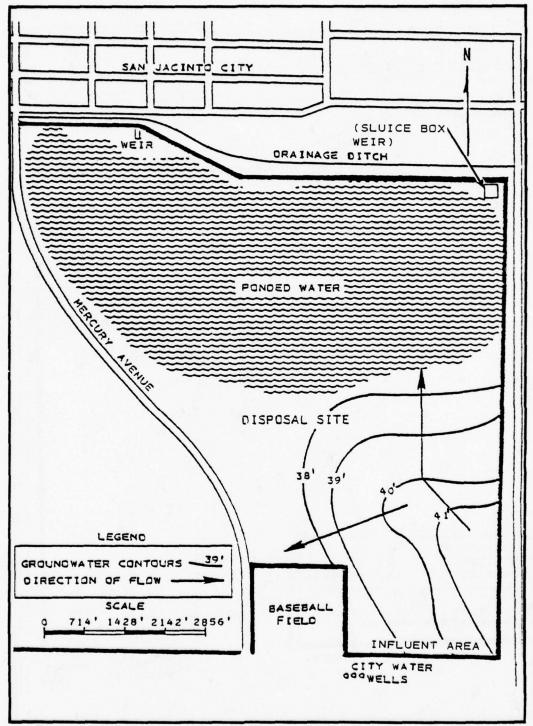


Figure 39 . Water level contours on November 6, 1976, Houston, Texas

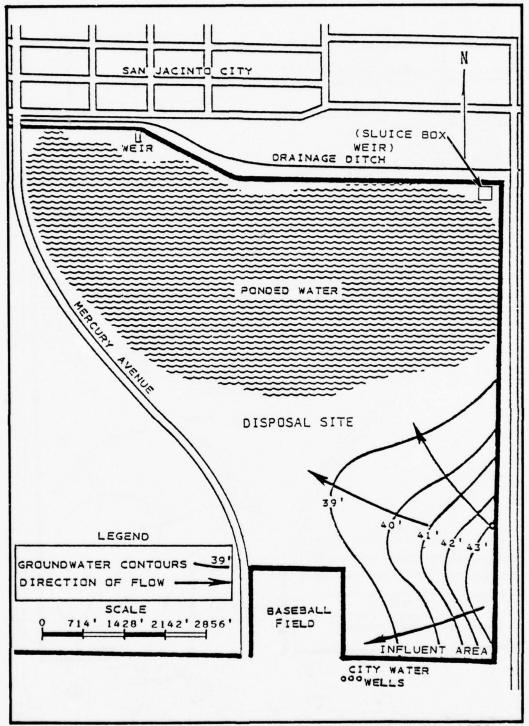


Figure 40 Water level contours on December 10, 1976, Houston site

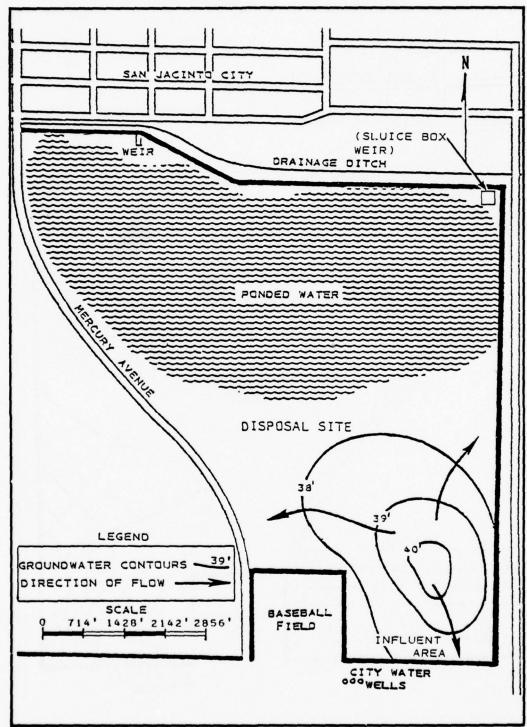


Figure 41. Water level contours on March 25, 1977, Houston site

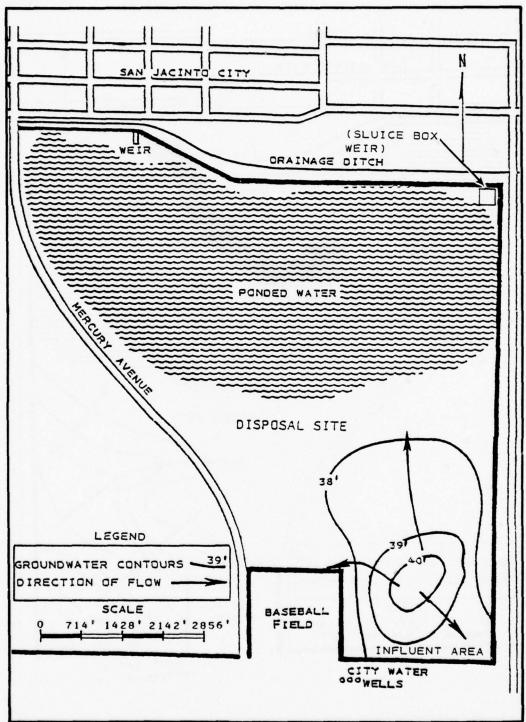


Figure 42. Water level contours on June 12, 1977, Houston site

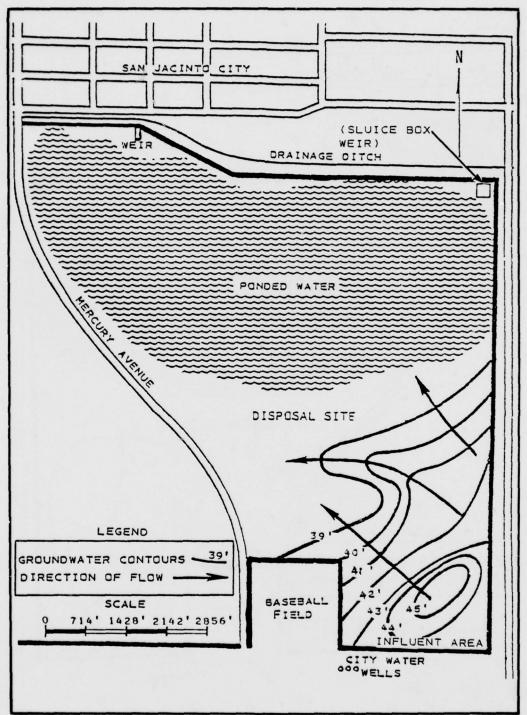
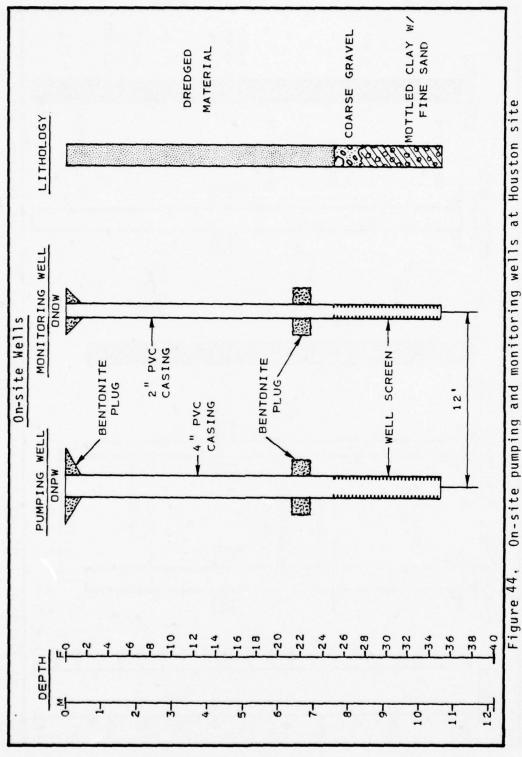
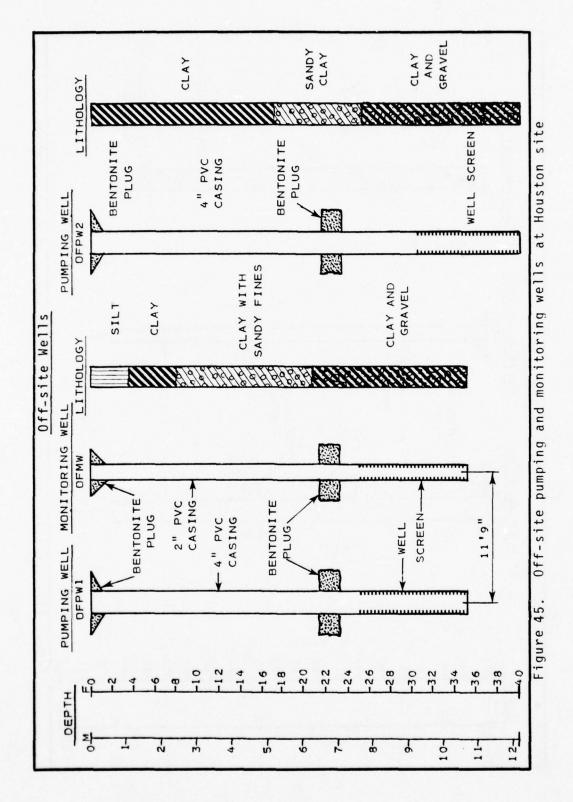


Figure 43. Water level contours on July 30, 1977, Houston site



On-site pumping and monitoring wells at Houston site



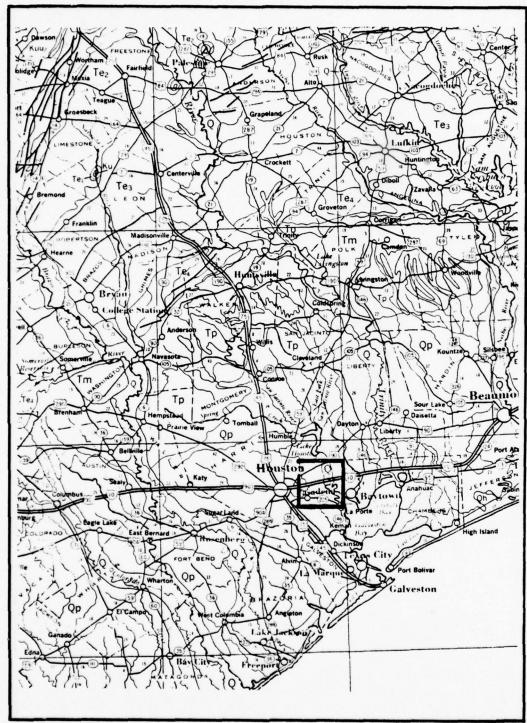


Figure 46. Geologic map of Houston area

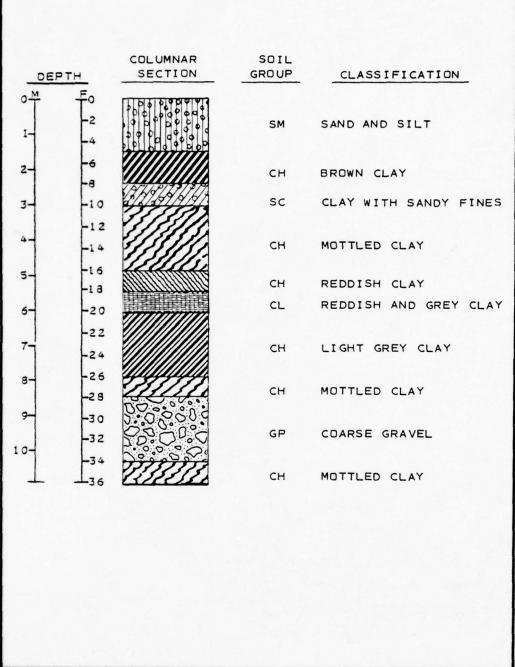
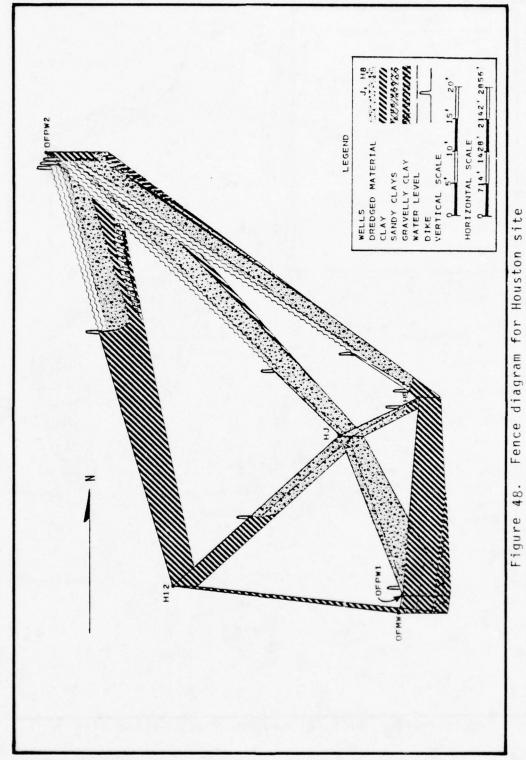


Figure 47. Generalized soil profile for Houston



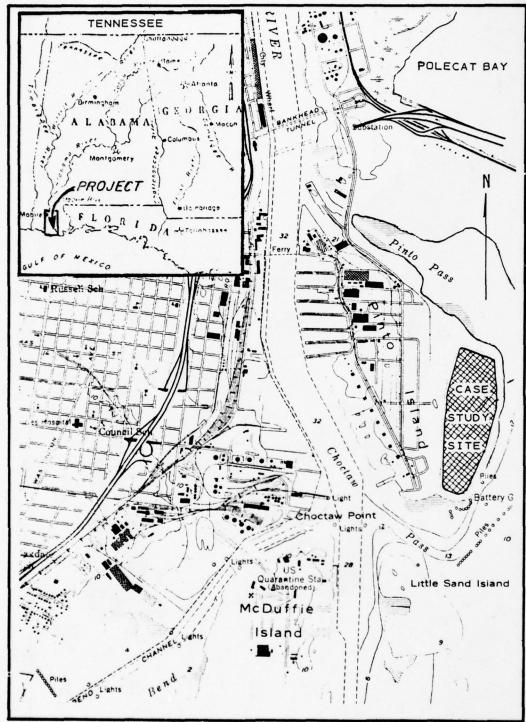


Figure 49. Regional map for Pinto Island site

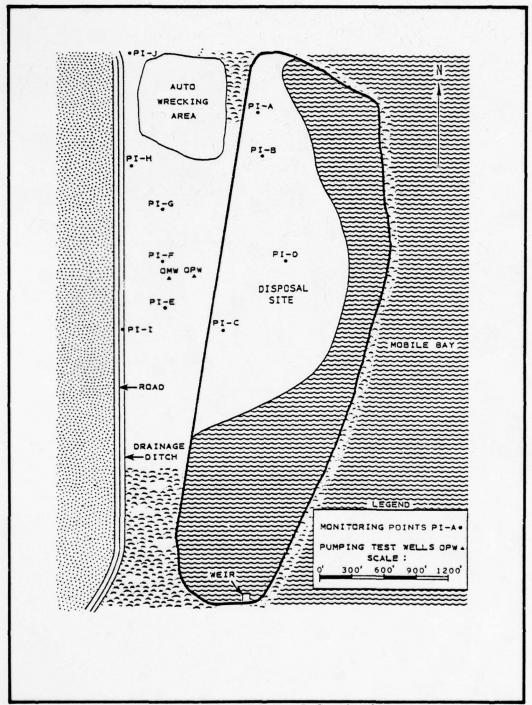


Figure 50. Pinto Island site

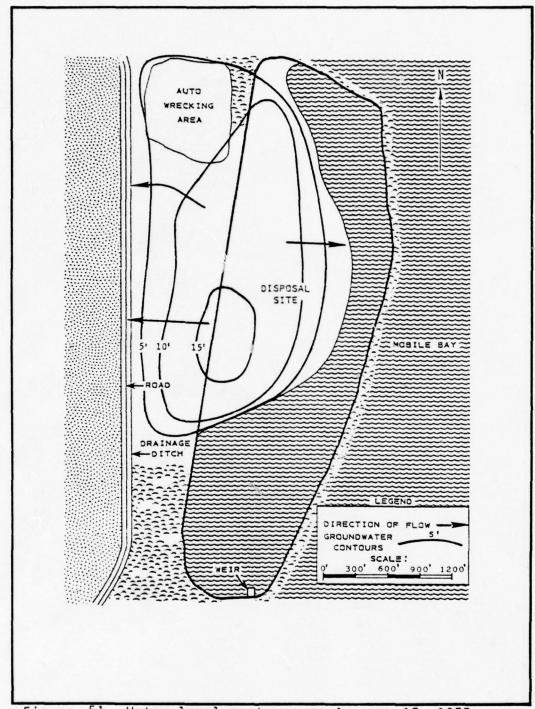


Figure 51. Water level contours on January 17, 1977, Pinto Island site

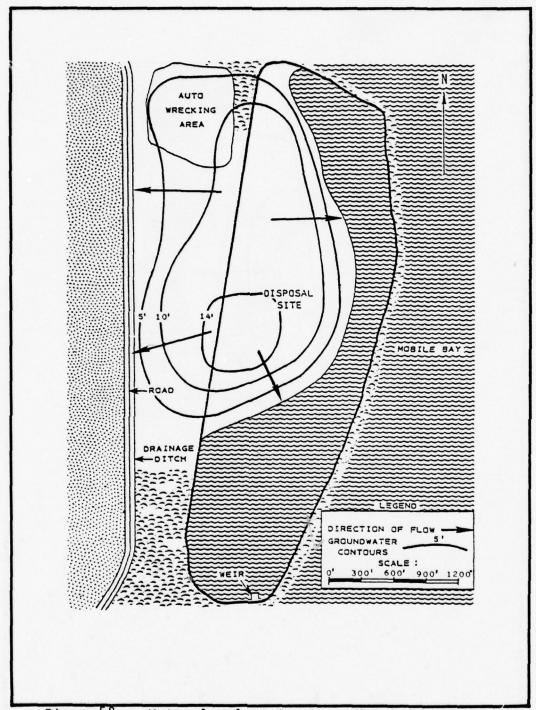


Figure 52. Water level contours on March 26, 1977, Pinto Island site

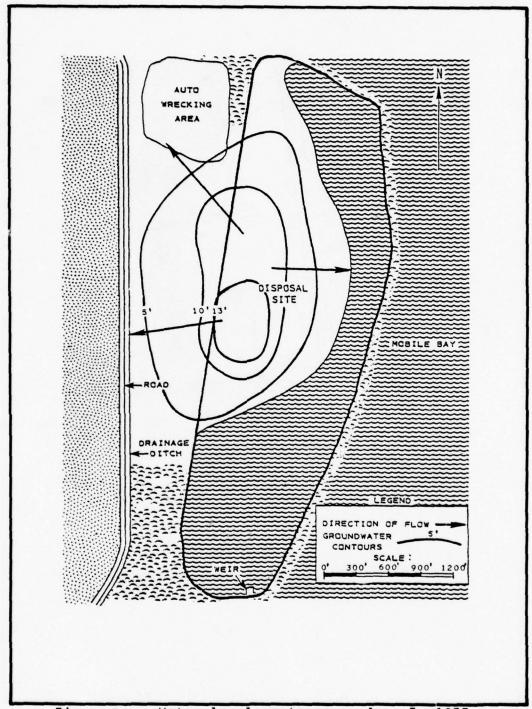


Figure 53. Water level contours on June 7, 1977, Pinto Island site

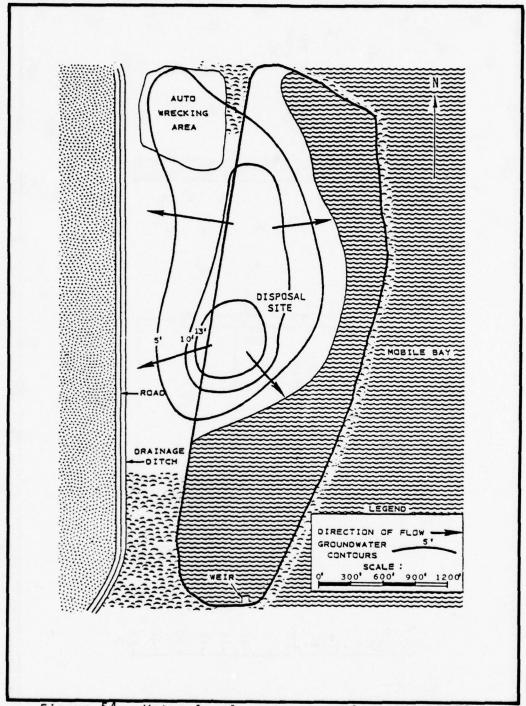
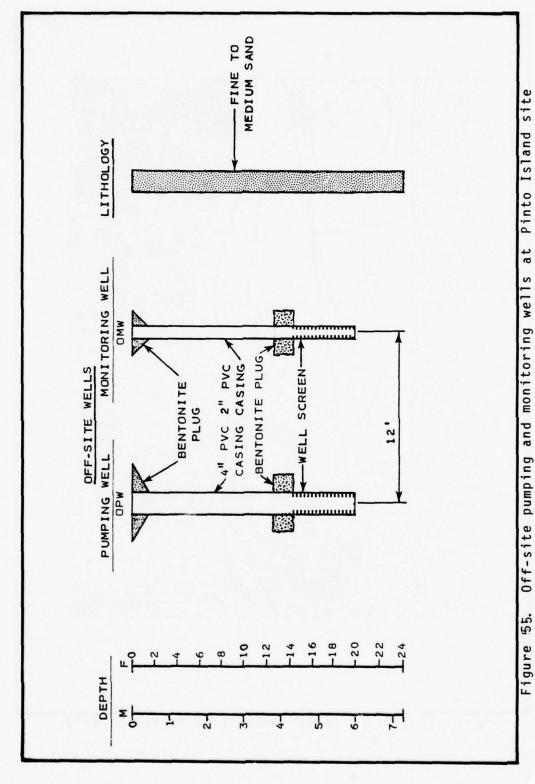
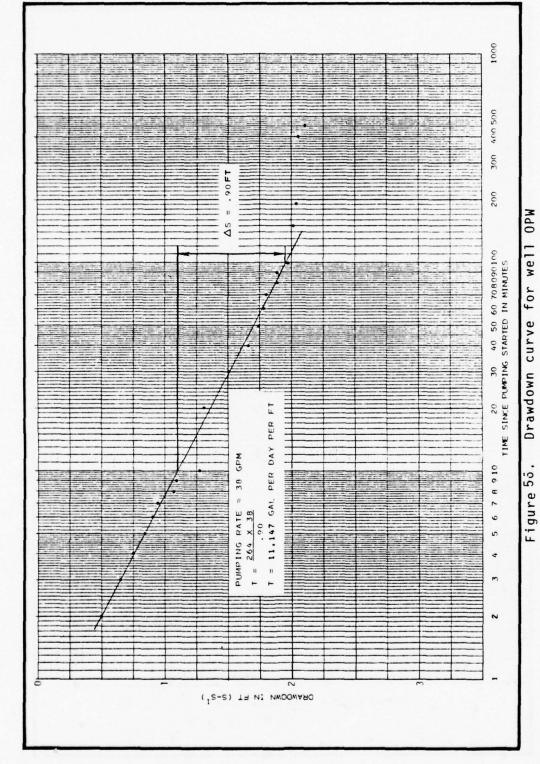
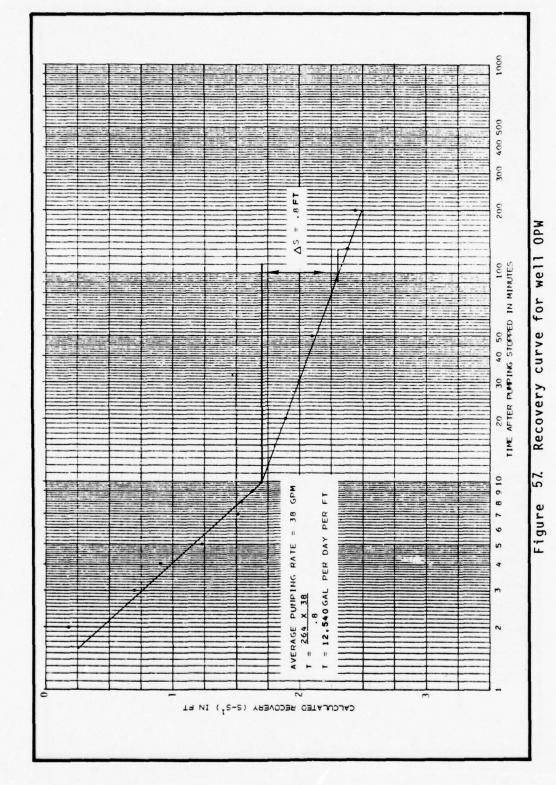


Figure 54. Water level contours on August 1, 1977, Pinto Island site







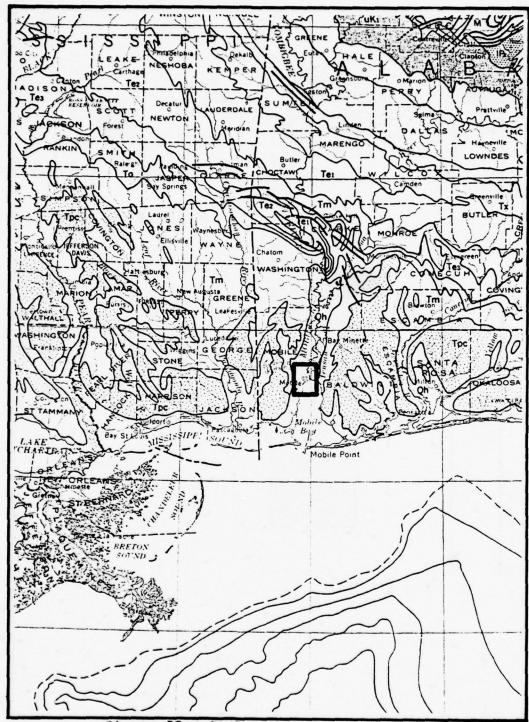


Figure 58. Geologic map of Mobile area

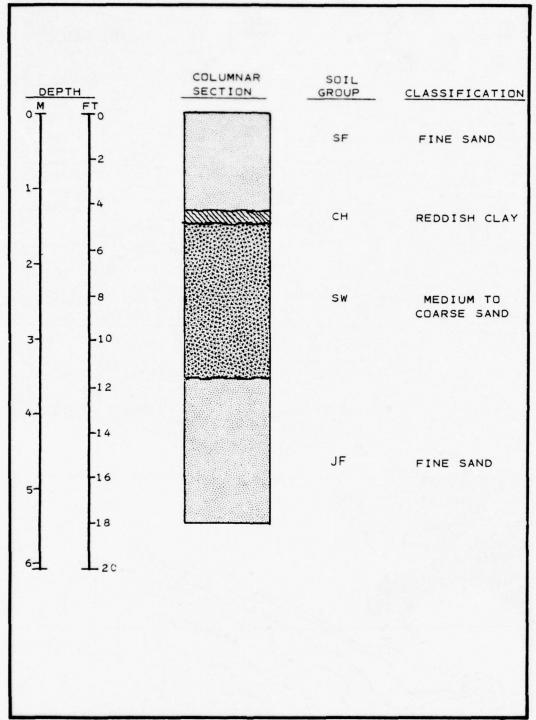
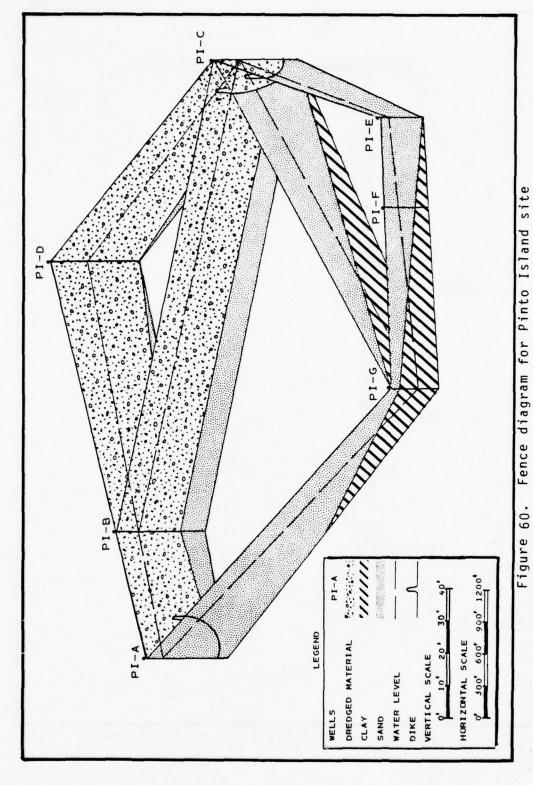


Figure 59. Generalized soil profile, Pinto Island site



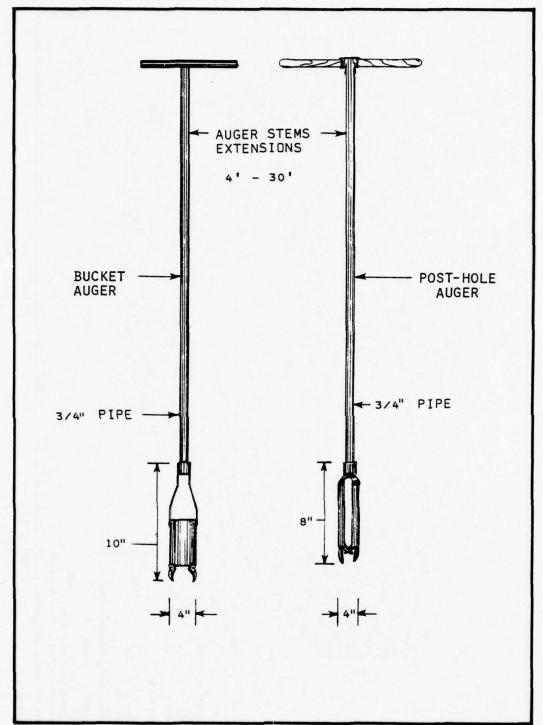


Figure 61. Bucket auger and post-hole auger

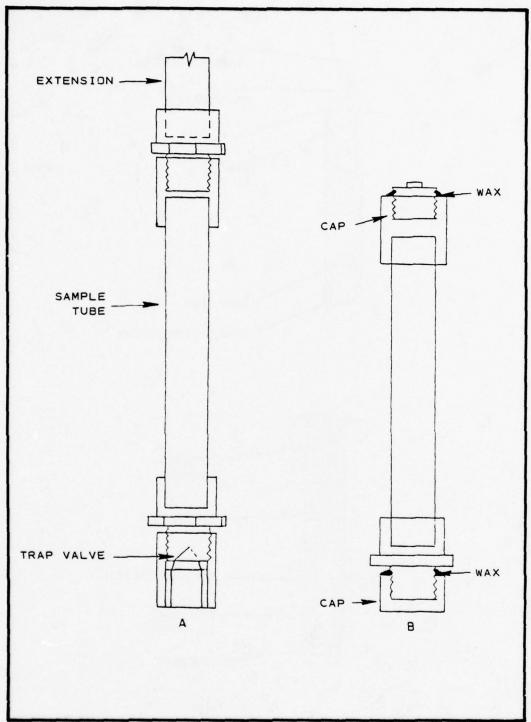


Figure 62 . Sampler and sample tube

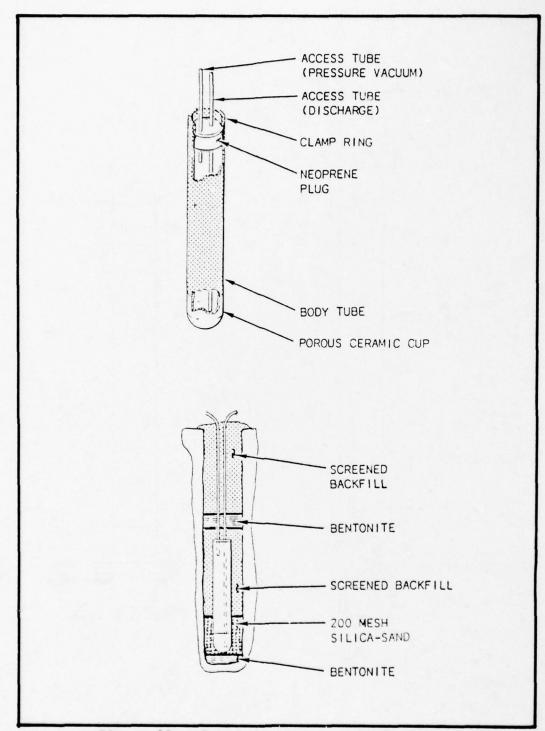


Figure 63. Pressure-vacuum soil lysimeter

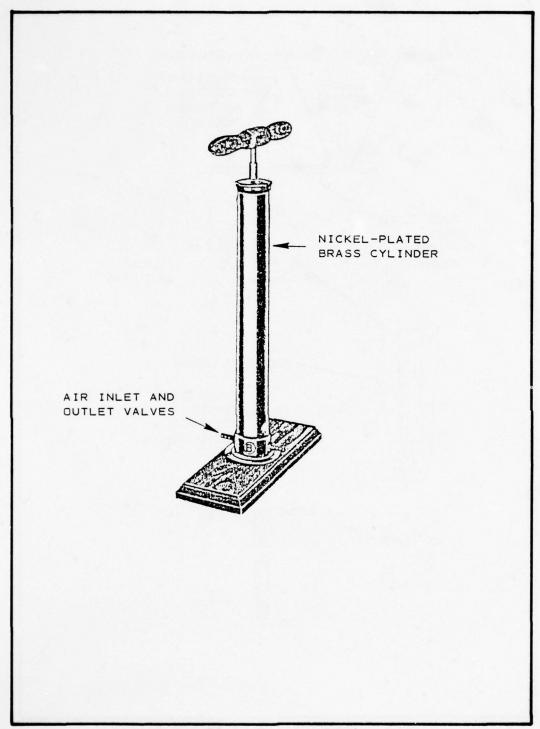


Figure 64 . Two-way hand pump

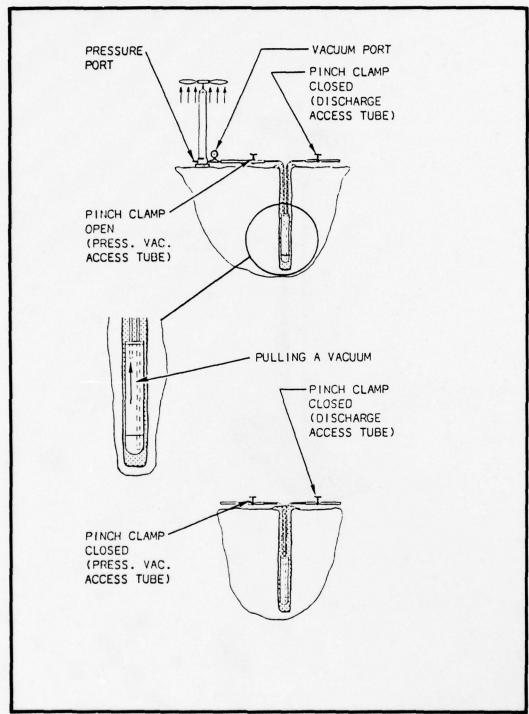


Figure 65 . Application of vacuum within pressure-vacuum lysimeter

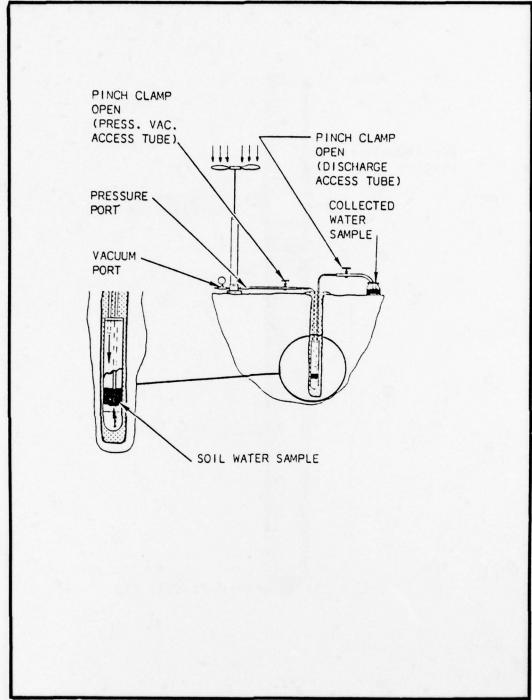


Figure 66. Collection of interstitial water from pressure-vacuum lysimeter

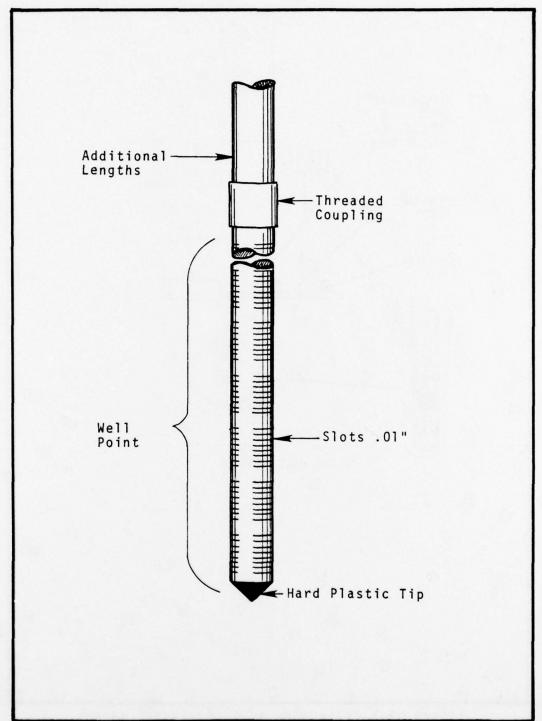


Figure 67. Plastic well point

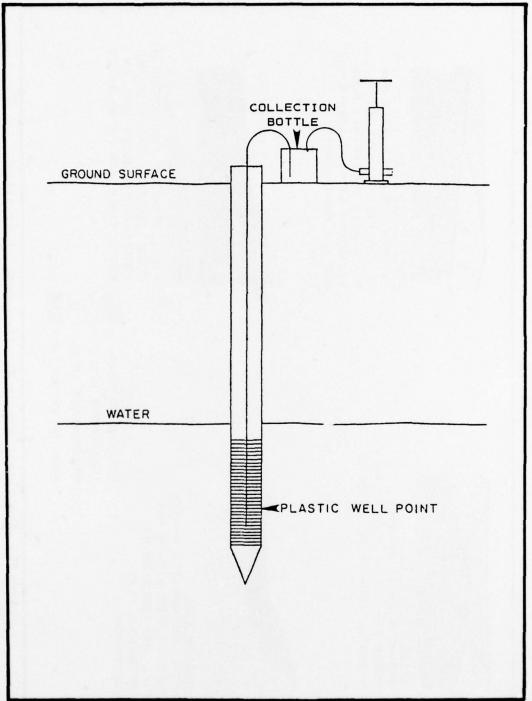


Figure 68. Procedure for collecting water from groundwater wells

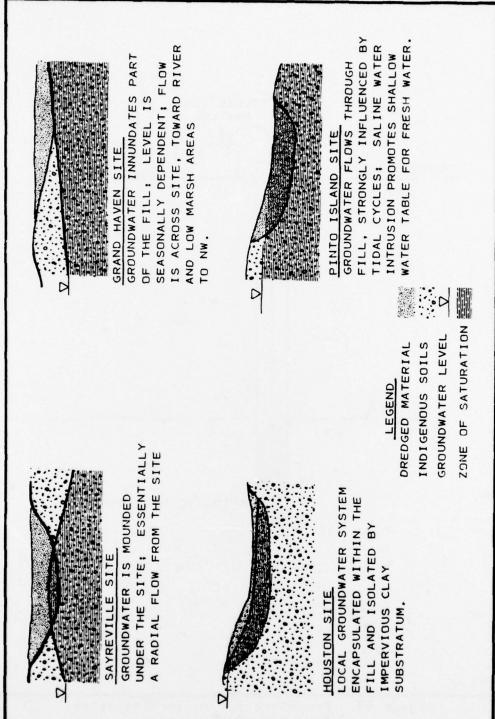
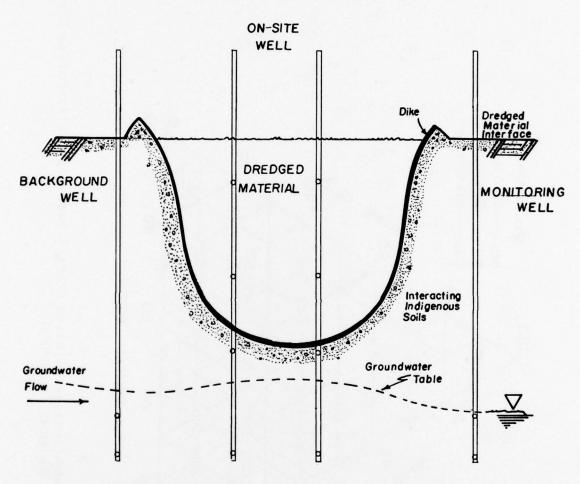


Figure 69. Hydrologic models for four case study sites



• - LYSIMETER LOCATION

Figure 70. General position of Samplers

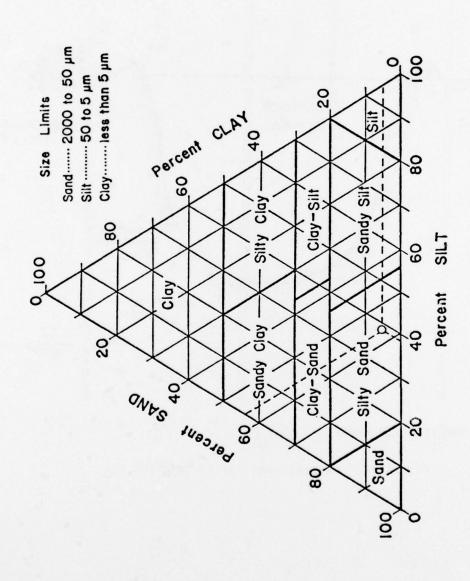


Figure 71  $\cdot$  Triangular classification chart (Lower Mississippi,Valley Division, corps of Engineers, U.S. Army)

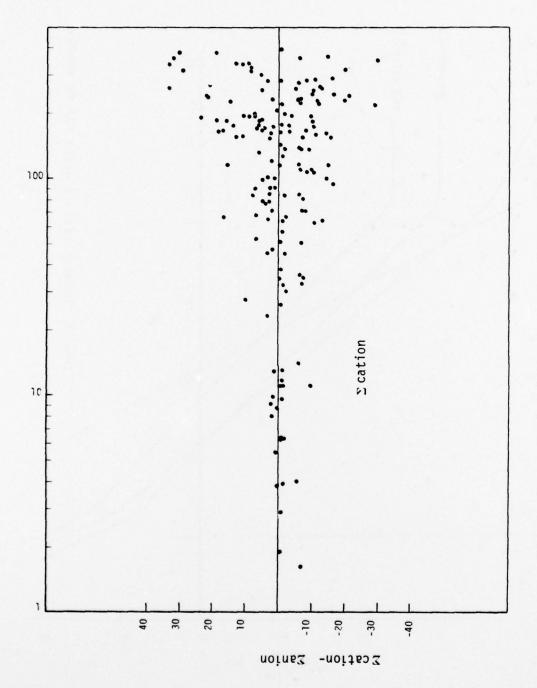
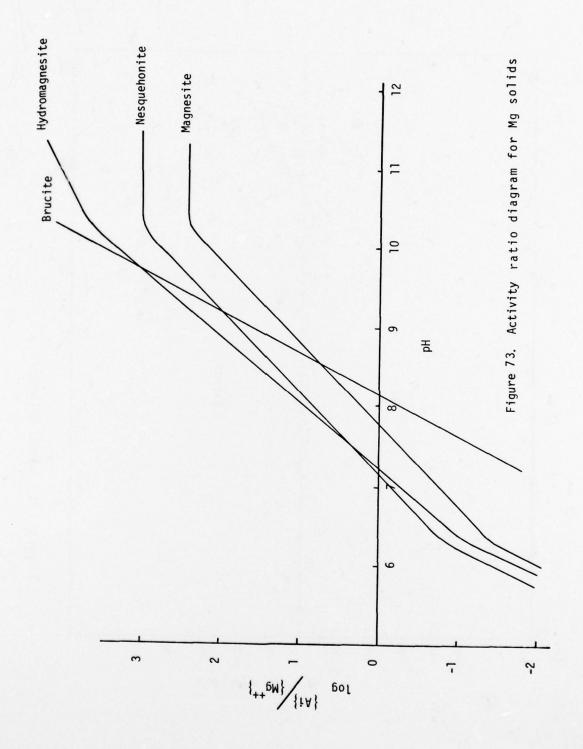


Figure 72. Ionic Balance



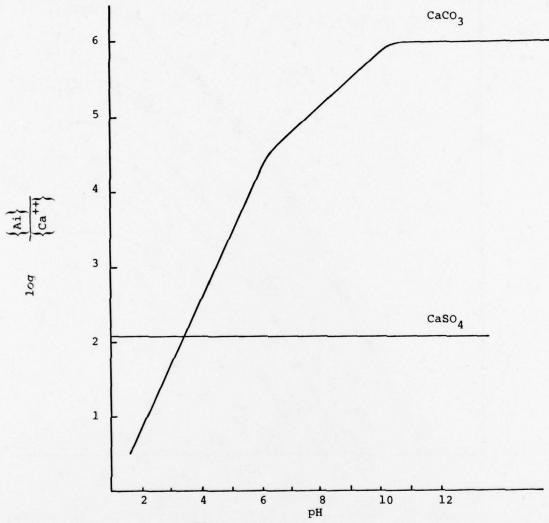


Figure 74. Activity ratio diagram for calcium solids

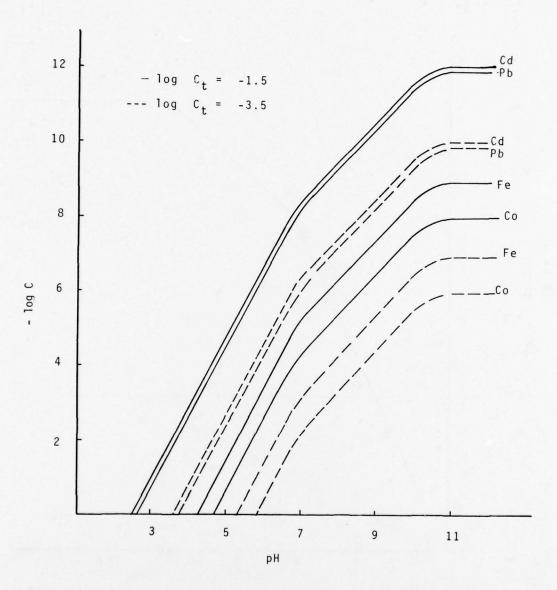


Figure 75. Solubility of Cd, Cu, Fe, Pb carbonates

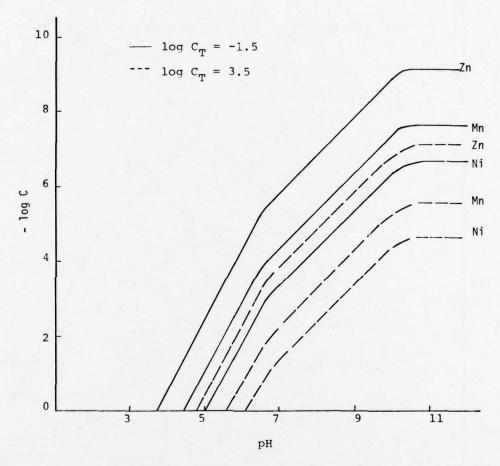


Figure 76. Solubility of Mn, Ni, and Zn carbonates

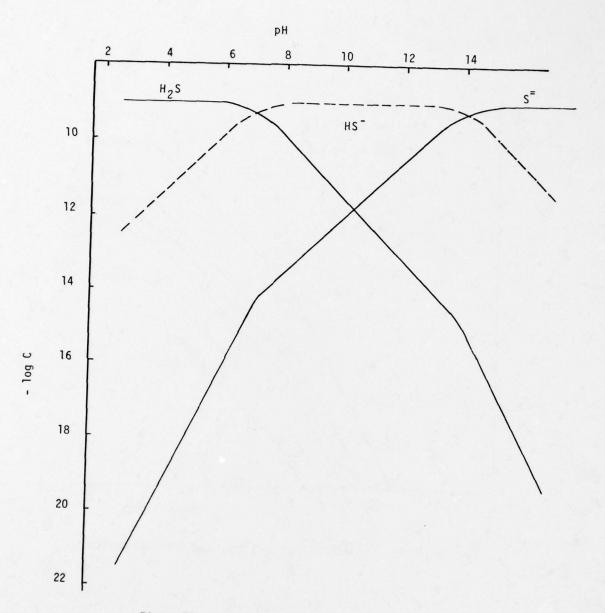


Figure 77. Distribution of sulfide species

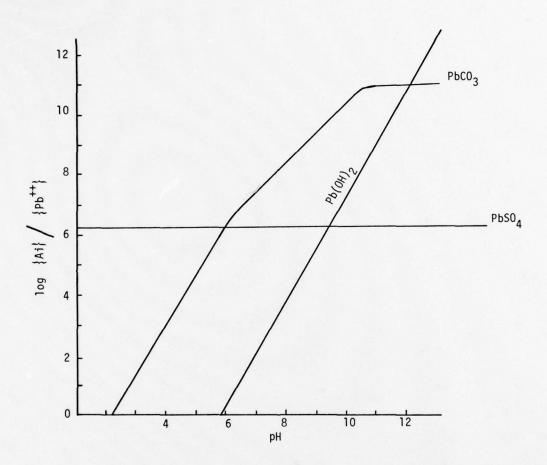


Figure 78. Activity ratio diagram for lead

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Yu, Kar Y

Physical and chemical characterization of dredged material sediments and leachates in confined land disposal areas / by Kar Y. Yu, Kenneth Y. Chen, Environmental Engineering Program, University of Southern California, Los Angeles, Calif., and Robert D. Morrison, James L. Mang, SCS Engineers, Long Beach, Calif. Vicksburg, Miss.: U. S. Waterways Experiment Station; Springfield, Va.: available from National Technical Information Service, 1978.

xiv, 241, [199] p.: ill.; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station; D-78-43)

Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C., under Contract No. DACW39-76-C-0171 (DMRP Work Unit No. 2005)

Appendices A-L on microfiche in pocket. References: p. 96-112.

1. Dredged material. 2. Dredged material disposal.

(Continued on next card)

Yu, Kar Y

Physical and chemical characterization of dredged material sediments and leachates in confined land disposal areas ... 1978. (Card 2)

3. Leachates. 4. Sediment. 5. Waste disposal sites. 6. Water quality. I. Chen, Kenneth Y., joint author. II. Mang, James L. joint author. III. Morrison, Robert D., joint author. IV. Los Angeles. University of Southern California. Environmental Engineering Program. V. SCS Engineers, Long Beach, Calif. VI. United States. Army. Corps of Engineers. VII. Series: United States. Waterways Experiment Station, Vicksburg, Miss. Technical report; D-78-43.